

A STUDY OF WATER-IN-OIL EMULSIFICATION

by

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ABSTRACT

The basic mechanism by which asphaltenes, resins, and waxes stabilize water-in-oil emulsions are examined. Experiments were conducted on the emulsification behaviour of model oils which consisted of an alkane component, an aromatic component, and the emulsifying agents. Results from this study clearly demonstrate the importance that the physical state of an emulsifying agent has upon its ability to stabilize emulsions. It was found that to be effective emulsifiers, asphaltenes, resins and waxes must be in the form of sub-micron particles. In addition, it was shown that the solvency strength of an oil, which is determined by its alkane and aromatic components, controls the solubility/precipitation behaviour of these emulsifiers. The chemical composition of the oil determines not only the amount and size of precipitated particles, but also the composition and wetting properties of the particles. All these factors were found to have an influence upon emulsification.

The potential application of a solubility model, using the Hildebrand-Scatchard equation, to predict the physicochemical conditions which favour water-in-oil emulsification, is discussed. Also, theories on various emulsification processes are discussed in terms of mousse formation at sea.

RESUME

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INTRODUCTION

It is well known that the emulsification of spilled oil into stable water-in-oil emulsions (chocolate mousse) has numerous detrimental effects upon clean-up operations. The increase in volume due to the incorporation of water means that the amount of polluted material that must be dealt with is multiplied several times. The viscous nature of mousse not only impedes the efficient operation of most mechanical recovery equipment, but it also results in a cohesive slick that resists dispersion, both natural and chemical. To a large extent, it is the rate at which spilled oil emulsifies that determines the effective window of opportunity for specific countermeasures.

Much has been learned from previous studies on petroleum emulsification (Bansbach 1970; Berridge Thew and Loriston-Clarke 1968; Bridie, Wanders, Zegveld and Vander Heijde 1980; Brown, Weiss and Goodman 1990; Canevari 1982; Desmaison, Piekarski and Desmarquest 1984; Eley, Hey and Symonds 1988; Eley, Hey, Symonds and Willison 1976; Graham 1988; Haegh and Ellingsen 1977; Jacob and Mackay 1977; Jones, Neustadter and Whittingham 1978; Lamathe 1982; Little 1981; Mackay 1987; Mackay and Zagorski 1982; Mackay, McLean, Betancourt and Johnson 1973; Payne and Phillips 1985; Thingstad and Pengerud 1983; Thompson, Taylor and Graham 1985; Walters and Fennell 1976) but it still remains a phenomenon that is poorly understood. Although most crude oils can be emulsified, not all spills result in the formation of stable mousse. Whether an oil will form mousse or not, and if so, at what rate, depends upon an array of different factors including the properties of the oil and the prevailing environmental conditions. The formation of mousse is the result of a complex series of processes. A better understanding of the emulsification process is desirable in order to better predict the emulsification behaviour of oil spills, and thus utilize the most appropriate countermeasures available.

The aim of this study was to elucidate the role that physico-chemical factors play in determining an oil's susceptibility to emulsify. This was done by studying the emulsification behaviour of oils of known composition, in order to examine the importance of oil chemistry in the emulsification process.

LITERATURE REVIEW

It has long been recognized that indigenous petroleum emulsifying agents are concentrated in the higher boiling fractions (boiling point $> 370^{\circ}\text{C}$) and particularly in the residuum (Lawrence and Killner 1948). It is generally accepted that asphaltenes, resins and waxes play key roles in the emulsion process but specific mechanisms have not been clearly established (Bridie, Wanders, Zegveld and Vander Heijde 1980; Canevari 1982; Mackay 1987). These compounds are believed to be the main constituents of the interfacial films which encapsulate the water droplets contained in mousse. These films have been shown to have high mechanical strength and thus act as effective physical barriers which prevent droplet coalescence (Blair 1960; Canevari 1982; Eley, Hey and Lee 1987; Hasiba and Jessen 1967; Jones, Neustadter and Whittingham 1978). This in turn gives rise to the stable nature of mousse.

Oil Chemistry

The main constituents of any oil can be grouped into four broad classes of chemicals. These being: Alkanes (also sometimes called saturates or aliphatics); Aromatics; Resins; and Asphaltenes. Previous studies have identified that asphaltenes, resins and waxes (which are part of the alkane group) play a role in emulsification. It is important to realize how these components are defined and to have an understanding of their basic chemistry. Different methods of separating these fractions from oil are likely to produce different materials.

Waxes

Simple definitions of petroleum wax are: the material in an asphaltene/resin-free oil which are insoluble in the solvent methyl ethyl ketone or insoluble in dichloromethane at 32°C. Another definition for petroleum wax is the high molecular weight paraffinic substances which crystallize out from an oil when cooled below the pour point. Petroleum wax is normally divided into two sub-categories: paraffin wax and microcrystalline wax. Paraffin waxes are normal alkanes with 20 to 40 carbon atoms and melting points from 32 to 71°C. Microcrystalline wax mainly consists of iso-alkanes with 35 to 75 carbon atoms and has a melting point from 54 to 93°C (Clark 1988).

Resins

Resins are complex high molecular weight compounds containing oxygen, nitrogen and sulphur atoms. They are polar and have strong adsorption tendencies. The term "resins" has been defined in various ways but it is generally considered to be the material that remains in solution after the asphaltenes have been removed by precipitation and which will adsorb onto surface-active material (such as Fuller's earth).

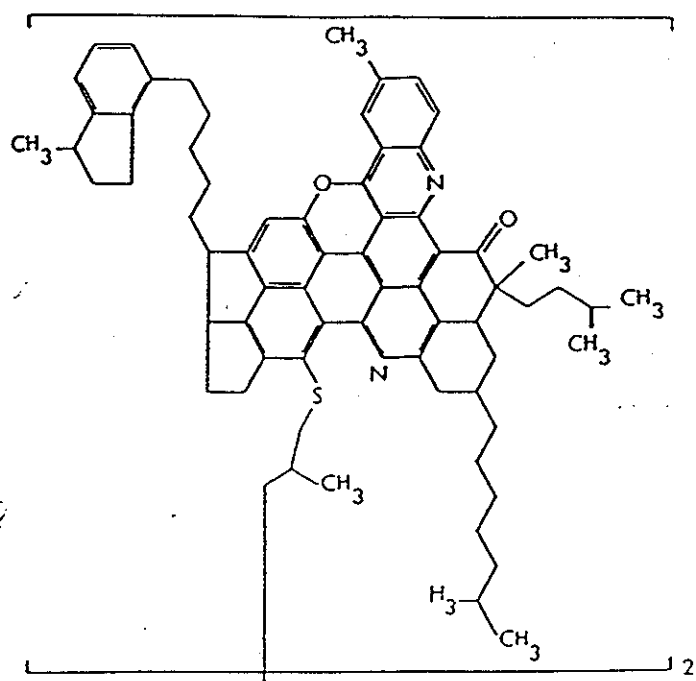
Petroleum resins are often considered to be low molecular weight asphaltenes but usually contain a higher percentage of saturated aliphatic and naphthenic structures in their molecules. Molecular weights of resins are assumed to range from about 800 to 1500.

Asphaltenes

Asphaltenes are defined by their solubility behaviour; asphaltenes are soluble in aromatic solvents and insoluble in alkane solvents. Asphaltenes are generally considered to consist of condensed aromatic nuclei which carry alkyl and alicyclic systems with heteroatoms (nitrogen, oxygen, sulphur, metals, salts) scattered throughout in various locations. Asphaltene molecules can have carbon numbers from 30 to over 40, and molecular weights from 500 to 10,000 have been cited in the literature. Asphaltenes are characterized by a C-H ratio of close to one and a specific gravity near one. Relatively little is known about asphaltene structures and much of the data is inferred. Figure 1 shows a hypothetical structure of an asphaltene (Speight 1981).

The physical nature of asphaltenes as they exist in petroleum is still speculative. One theory that is generally accepted is that petroleum should be viewed as a colloidal system. Asphaltene molecules agglomerate to form clusters similar to micelles. These asphaltene micelles interact with the resins which in turn peptize the asphaltenes and enables a stable colloidal dispersion to exist. Since these colloids contain most of the polar material found in the oil, they essentially determine the interfacial properties (Clark 1988; Long 1979; Speight 1981; Neumann et al. 1981).

Figure 1: Hypothetical structure of a California Crude oil asphaltene.



Solubility Theory

In a complex mixture like petroleum, the compounds interact in such a way that all components are maintained in the liquid oil phase. From a simple viewpoint, the lighter components of the oil act as solvents for the higher molecular weight compounds. As long as this solvency interaction is maintained in the oil and thermodynamic conditions remain constant, the oil will remain stable. Should this equilibrium state be changed, a point will be reached where the solvency strength of the oil is insufficient to maintain the heavy components in solution and as a result, they will precipitate out as solid particles. This is a frequent and problematic occurrence seen during petroleum production, transportation, and storage (Griffith and Siegmund 1985; Kawanaka, Leontaritis, Park and Mansoori 1989; Majeed, Bringedal and Overa 1990; Mochida, Sakanishi and Fujitsu 1986).

The precipitation of asphaltenes and waxes from oil has been modelled by several researchers (Griffith and Siegmund 1985; Kawanaka, Leontaritis, Park and Mansoori 1989; Majeed, Bringedal and Overa 1990) using the basic solubility theory as described by the Hildebrand-Scatchard equation (Barton 1983). In this case, oil is viewed as being comprised of a solute and a solvent. If one uses the solubility/precipitation behaviour of asphaltenes, the solute consists of the asphaltenes and the solvent consists of the remaining compounds in the oil. The solubility behaviour of asphaltenes in petroleum is:

$$RT \ln (A_a / X_a) = \frac{M_a \phi_s^2 (\delta_a - \delta_s)^2}{P_a}$$

where:

- A_a = activity coefficient of asphaltenes
- X_a = mole fraction of asphaltenes
- M_a = molecular weight of asphaltenes
- ϕ_s = volume fraction of solvent
- δ_a = Hildebrand solubility parameter of the asphaltenes
- δ_s = Hildebrand solubility parameter of the solvent
- p_a = density of asphaltenes
- R = gas constant
- T = temperature

With the assumption that asphaltenes are a homogeneous material and that $A_a = 1$, the above equation can be re-written in terms of the maximum amount of asphaltenes soluble in the oil, X_a .

$$\ln X_a = \frac{-M_a \phi_s^2 (\delta_a - \delta_s)^2}{p_a RT}$$

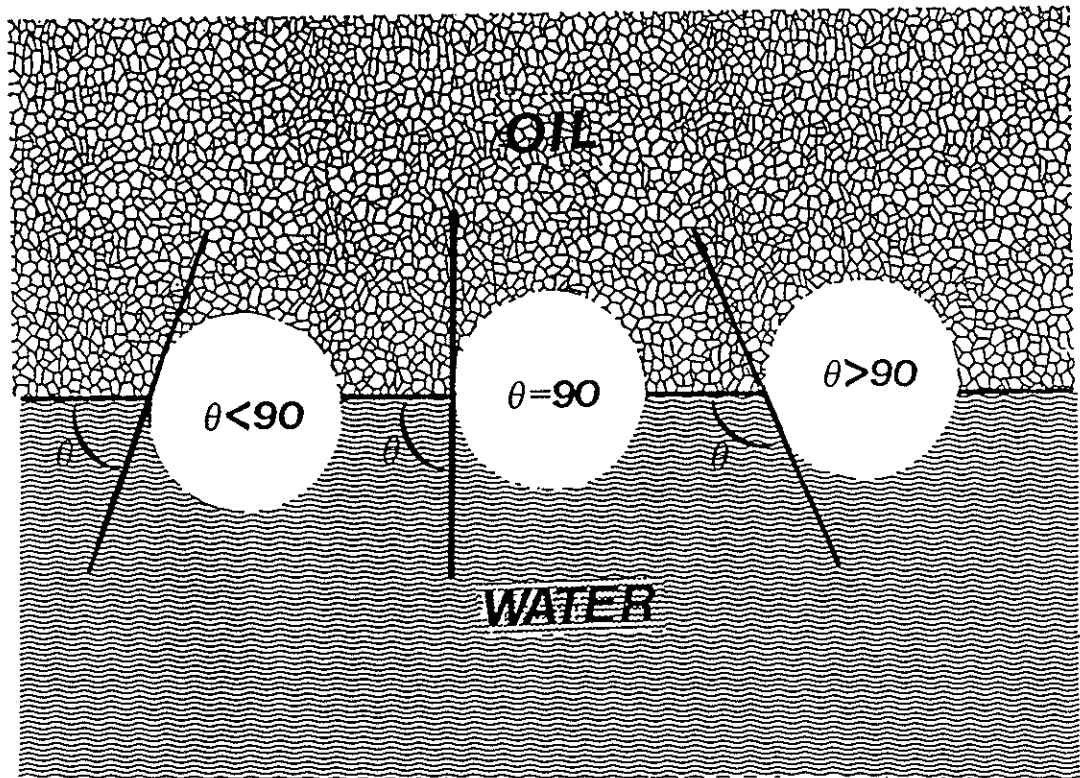
If the amount of asphaltenes present in the oil exceeds X_a , the excess asphaltenes will precipitate.

Particles as Emulsifiers

The role of solid particles in petroleum emulsification has been recognized for some time (Van der Waarden 1958), however the importance of this mechanism to mousse formation has not been completely appreciated. Examination of crude oil mousse using an electron microscope, clearly showed particles in the interfacial film surrounding water droplets (Eley, Hey, Symonds and Willison 1976). Thompson et al. (Thompson, Taylor and Graham 1985) showed that wax particles and associated solids exert considerable influence upon the emulsion stability of a waxy North Sea crude. They found that removing the indigenous particles from this oil inhibited the oil's tendency to form stable emulsions. Similarly, Eley et al. (Eley, Hey and Symonds 1988) demonstrated that by varying the aromatic/aliphatic character of a synthetic oil containing asphaltenes, they could control the extent of emulsification.

For solids to act as emulsifying agents, the particles must possess certain properties. The particles must be very small relative to the droplet size of the emulsified phase. The particles must collect at the interface and they must be 'wetted' by both the oil and water phases. Figure 2 shows three ways that particles may distribute themselves between an oil-water interface. If the particle is preferentially wetted by the oil, the contact angle between the oil-water-solid boundary, θ , is greater than 90° and a water-in-oil emulsion will form. If the particle is preferentially wetted by water, θ is less than 90° and an oil-in-water emulsion will form. If the contact angle is much greater or lesser than 90° , the emulsion will be unstable. Stable emulsions form when the contact angle is near 90° (Becher 1983; Canevari 1982).

Figure 2: Three ways solid particles may be distributed in an oil-water interface. The particle on the left is more wetted by the water than the oil thus being situated primarily in the aqueous phase, whereas the particle to the right exists primarily in the oil phase. The center situation illustrates a solid particle equally wetted by both the oil and water phases.



EXPERIMENTAL SECTION

The model oils used in these experiments consisted of three main components: 1. an alkane component; 2. an aromatic component; and 3. the potential emulsifying agent(s). Four different alkane components were tested: n-octane, n-tetradecane, a light paraffin oil, and a heavy paraffin oil. Paraffin oils are refined mixtures of alkanes. Aromatic components tested were p-xylene, phenyl octane, dimethyl naphthalene, and diphenyl methane. Asphaltenes, resins and waxes were used as emulsifying agents, either individually or in combinations. Asphaltenes were precipitated from a California crude oil (API gravity: 11) using 40 parts of n-pentane to one part of oil (Speight 1981). Asphaltenes and resins were precipitated together from the California crude using ethyl acetate (Neumann et al. 1981). Resins were precipitated from de-asphaltized oil using ethyl acetate. Precipitated materials were collected on a 0.45 micron filter, dried by a nitrogen purge, and stored in the dark under a nitrogen headspace. Other materials used were paraffin wax (Aldrich Chemical Company, melting point: 56-61°C) and graphite powder (Aldrich Chemical Company).

Model oils were prepared by adding the emulsifying agent to the aromatic component. The mixture was vigorously shaken for one hour. The alkane component was then added and the mixture was again shaken for one hour. 30 mL of the oil was poured into a 500 mL Fleaker containing 300 mL of artificial seawater. The Fleaker was stoppered and allowed to stand for approximately 20 hours before being subjected to the emulsion formation and stability test (Bobra 1989). This test involves rotating the Fleaker at 65 rpm for one hour and then allowing the mixture to remain static for one-half hour before measuring the size of the emulsion and the fraction of oil that emulsifies, F . The rotation/rest cycle is repeated three more times. An indication of an oil's tendency to emulsify is given by F_0 , the fraction of oil that emulsifies when F is extrapolated to time zero. The stability of the emulsion is obtained by allowing the emulsion to stand for 24 hours and then measuring the fraction of oil that remains in the emulsion, F_{final} . The water content of stable emulsions was also measured.

The following criteria set by Mackay and Zagorski (Mackay and Zagorski 1982) classify emulsion behaviour:

F_o -----	Emulsion formation tendency -----
0 to 0.25	not likely
0.25 to 0.75	fairly likely
0.75 to 1	very likely

F_{final} -----	Emulsion stability -----
0 to 0.25	unstable
0.25 to 0.75	fairly stable
0.75 to 1	very stable

The rheological properties of stable emulsions were measured using a Haake RV20 Rotoviscometer equipped with a M5/SV1 sensor. The programmed shear rate was 0 to 100 (s^{-1}) in 10 minutes and 100 to 0 (s^{-1}) in 10 minutes. The yield point values were determined from the increasing shear rate curves. The yield point can be considered to be an indication of the "solid" character of the emulsion. It is a measure of the force that must be applied to a emulsion in order to induce liquid flow. For the sake of comparison, under these same shear conditions mayonnaise has a yield point of 114 Pa and two samples of 18 day-old mousse from the Valdez spill had values of 17 and 121 Pa.

The size distribution of water droplets were determined using a Lab-Tec 1000 particle size analyser and a Zeiss Axioskop light/fluorescence microscope.

All experiments were conducted at 15°C.

RESULTS AND DISCUSSION

Asphaltenes as Emulsifying Agents

Figure 3 shows that the amount of asphaltenes precipitated out of the model oil is determined by the alkane/aromatic ratio of the oil, which on the graph is expressed as percent alkane in the oil. The alkane component of this particular oil series is the heavy paraffin oil, the aromatic component is xylene, and the asphaltene concentration is 0.05 g/mL. When these oils are subjected to the emulsification test, differences in the tendency to form stable emulsions are clearly evident as seen in Figure 4. The emulsion formation tendency of the oil as a function of alkane content is presented in Figure 5. There is a strong tendency ($F_o = 1$) for this oil to emulsify when the alkane content is between 50 and 95%. As shown in Figure 6, these emulsions are very stable ($F_{\text{Final}} > 0.75$), and as shown in Figure 7, they have water contents between 50 and 90%. Yield point data are given in Figure 8. The results show that there is a maximum yield point value reached when the model oil contains 80% alkane/20% aromatic. Rheologically, this emulsion is the most stable emulsion formed for this series of model oil. It can be inferred that at this point in the oil's composition, the asphaltene particles have the optimum size and contact angle with the interface to form emulsions. For the sake of comparison, two samples of mousse taken 18 days after the Exxon Valdez spill had yield points of 17 and 121 Pa under the same shear conditions.

Figure 3: Percent of asphaltenes precipitated out of solution as a function of the alkane content of the oil.

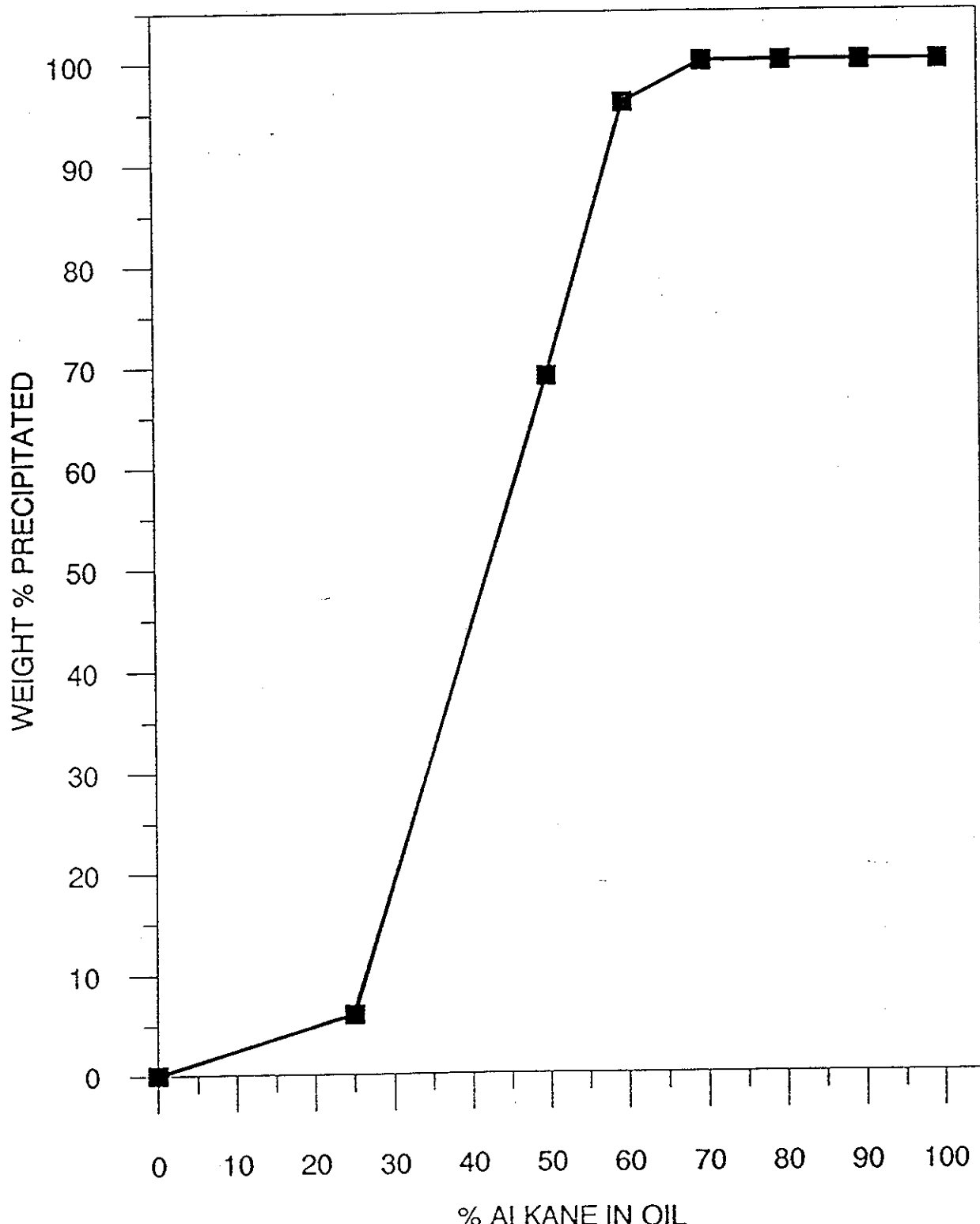


Figure 4: Appearance of model oils after undergoing the emulsion test.

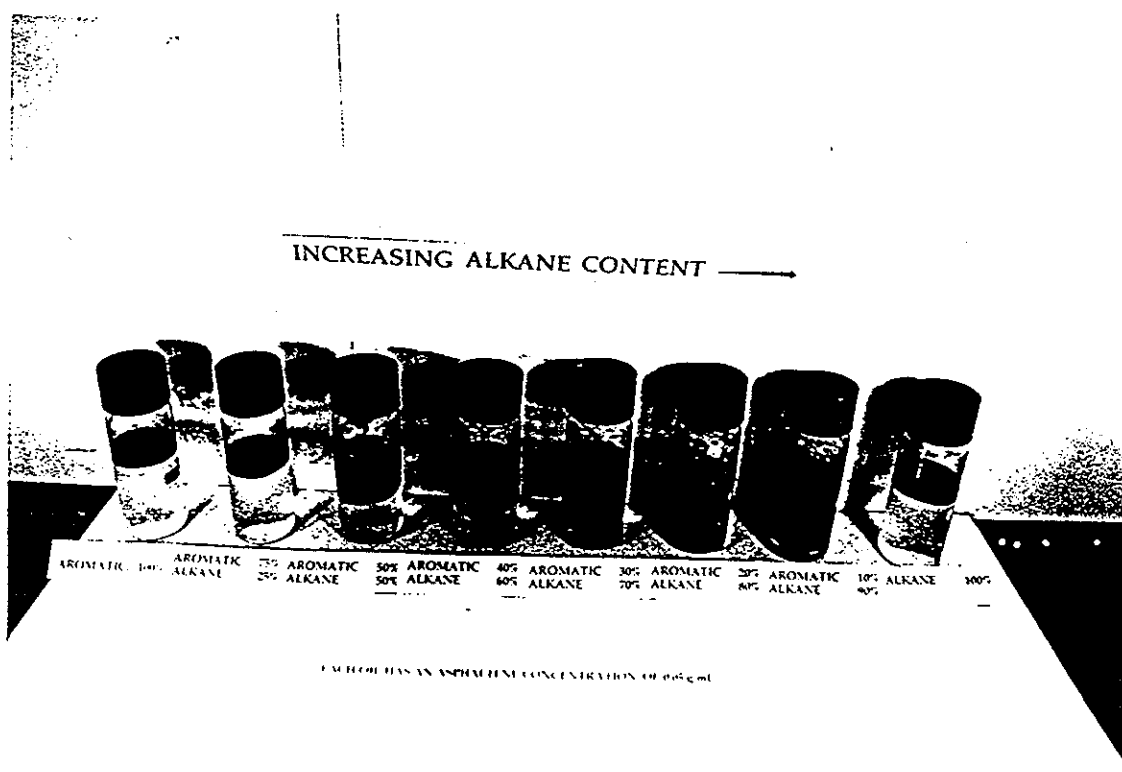


Figure 6: Emulsion formation stability, F_{Final} as a function of the alkane content of the oil. $F_{Final} = 0$ means emulsion completely broke after 24 hours. All oil remains emulsified if $F_{Final} = 1$.

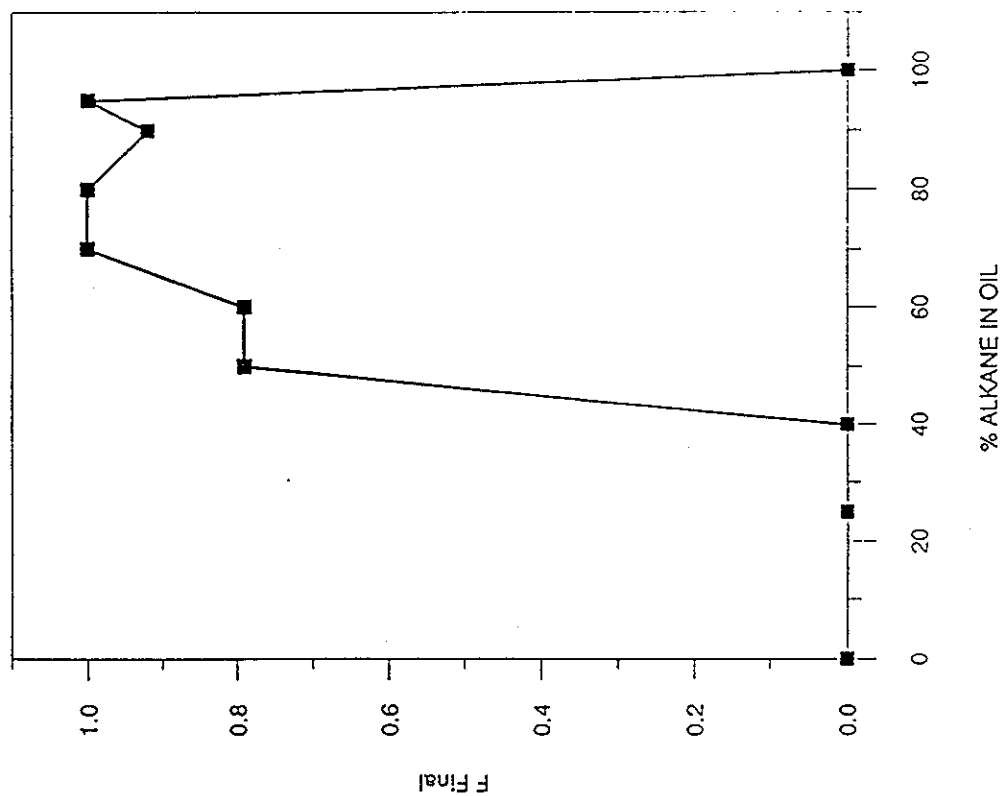


Figure 5: Emulsion formation tendency, F_o as a function of the alkane content of the oil. $F_o = 0$ means there is no tendency to emulsify, and $F_o = 1$ represents a strong tendency.

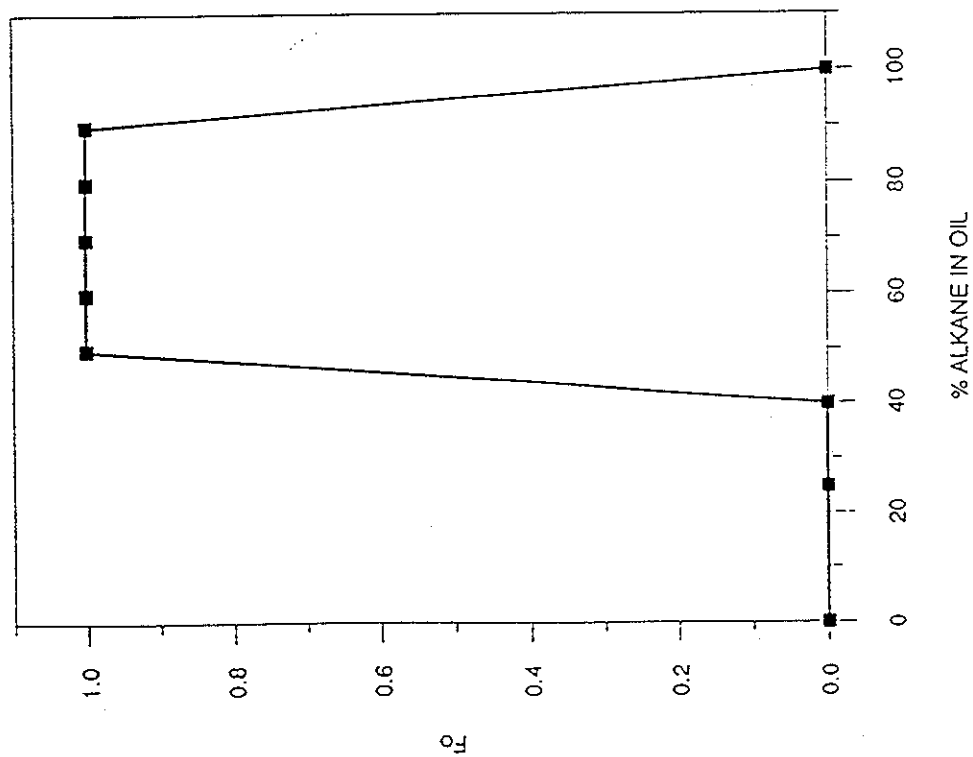


Figure 8: Yield point of stable emulsions formed versus % alkane in oil.

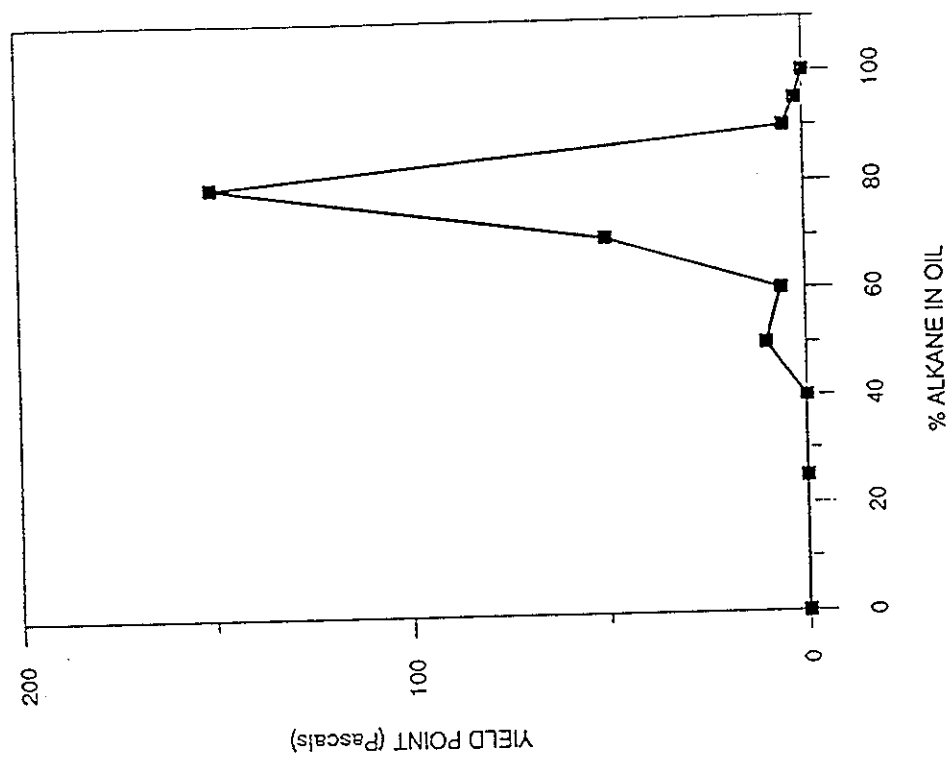
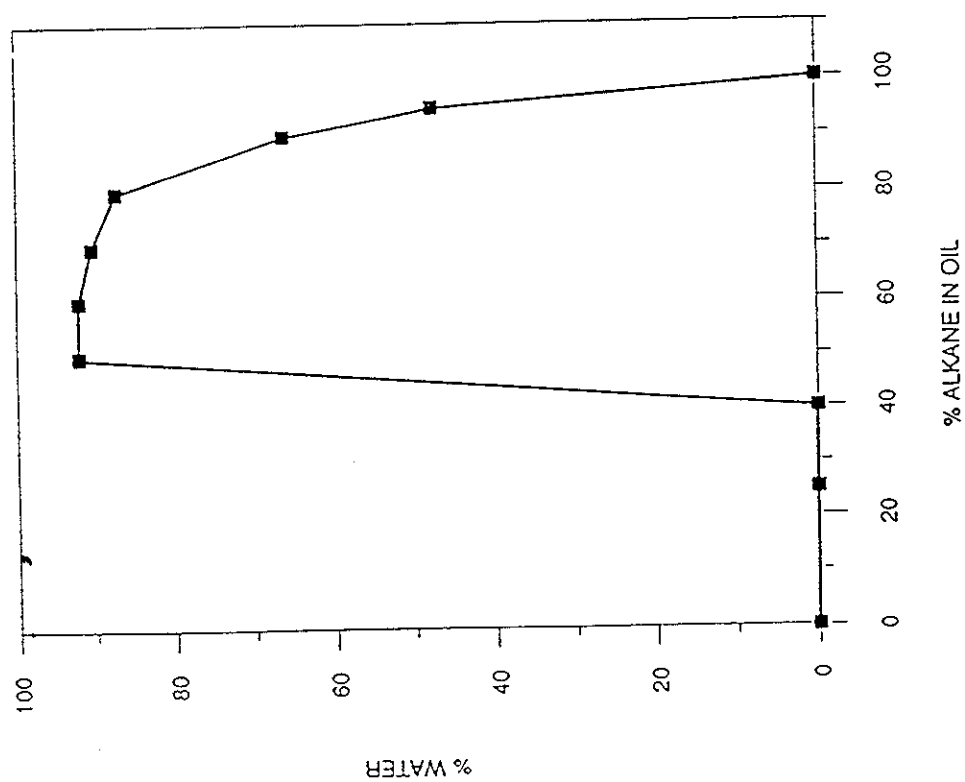


Figure 7: Water content of stable emulsions formed versus % alkane in oil.



Figures 9 to 12 show the influence of the alkane/aromatic ratio and the influence of increasing asphaltene content upon F_o , F_t , water content and yield point. The alkane component is heavy paraffin oil and the aromatic component is xylene. At an asphaltene concentration of 0.01 g/mL, no stable emulsions are formed. At an asphaltene concentration of 0.025 g/mL, the model oil has a tendency to emulsify ($F_o = 1$) when the oil is 50% alkane and 50% aromatic, and this emulsion is only marginally stable ($F_t = 0.5$). When the asphaltene content is increased to 0.05 g/mL, stable emulsions are readily produced for oils containing 50 to 95% alkane component. Likewise, at an asphaltene concentration of 0.1 g/mL, stable emulsions form for oils containing 35 to 80% alkane. Figure 11 shows that the water content of stable emulsions are between 80 to 90%. The change in yield point as a function of alkane composition, Figure 12, clearly shows that there is a maximum value for each concentration of asphaltenes. For oils containing 0.05 g/mL asphaltenes this maxima occurs at 80% alkane, and for oils containing 0.10 g/mL asphaltenes this occurs at 90%.

The results illustrate several important points concerning the influence of the alkane/aromatic ratio upon an oil's emulsification behaviour. The amount of asphaltenes precipitated out of solution is determined by the alkane/aromatic ratio of the oil. Clearly, this is important in determining the emulsification of the oil. Results from experiments where different concentrations of asphaltenes were used, indicate that a minimum particulate concentration of about 0.03 g/mL must exist in the oil for stable emulsions to form. But it would also appear that the alkane/aromatic ratio controls other factors which are involved in emulsification. The size of the asphaltene particles is determined by the alkane/aromatic ratio and this is particularly true given the method by which these model oils were prepared. Asphaltenes were first dissolved in the appropriate quantity of xylene and then the paraffin oil was added, this causes the asphaltenes to precipitate out of solution. When the model oil is predominantly composed of alkane (i.e. 100% alkane), this precipitation mechanism does not occur, and the asphaltenes maintain their original dimensions which are aggregates of approximately one micron. These particles are too large to effectively stabilize water droplets. This was confirmed by microscopic examination of the oils. When model oils which were prone to emulsification were

examined under the microscope, individual particle sizes could not be accurately determined because the particles were at the limit of resolution (<0.5 microns). But it could be seen that collectively the particles formed a continuous layer of finely dispersed particulates which are closely packed together. As the alkane content of the oil increased, the particles became more tightly packed. An interesting phenomenon was observed when model oils with high aromatic content were viewed under the microscope. The actual precipitation of asphaltenes could be observed as the oil evaporated under the intense light source. Particles would precipitate out in a uniform distribution covering the slide with a film of sub-micron particles.

Figure 13 shows that the addition of asphaltenes to the alkane/aromatic mixtures lowers the interfacial tension. However, an additional increase in the concentration of asphaltenes has no apparent effect on the interfacial tension. This illustrates that when particulates are the emulsifying agent, extreme lowering of interfacial tension is not required to form emulsions, as is the case with typical surfactants (Becher, 1983). It would appear that changes in interfacial tension have little to do with the emulsification behaviour of the model oils.

It would be expected that the alkane/aromatic ratio will have some effect on the contact angle between the particles and the interface, since oil composition will influence the wettability of particles. A simple experiment was performed which demonstrated the importance of the alkane/aromatic ratio on the contact angle. A series of oils of the same alkane/aromatic composition as previously tested were prepared and subjected to the emulsification test but instead of asphaltenes, graphite powder (0.05 g/mL) was used as the emulsifying agent. Graphite is insoluble in both xylene and paraffin oil. Therefore, there will be no changes in its physical form. The results from this experiment showed that stable emulsions ($F_{\text{Final}} = 1$) only formed at when the oil's composition was 50% alkane-50% aromatic. Unfortunately, facilities to measure contact angle were not available and therefore, this effect of alkane/aromatic ratio upon contact angle, and in turn upon emulsification, could not be substantiated. However, the results strongly imply that this influence upon contact angle is an extremely important determinant for emulsification by solid particles.

Figure 9: F_0 versus % alkane
at different asphaltene concentrations

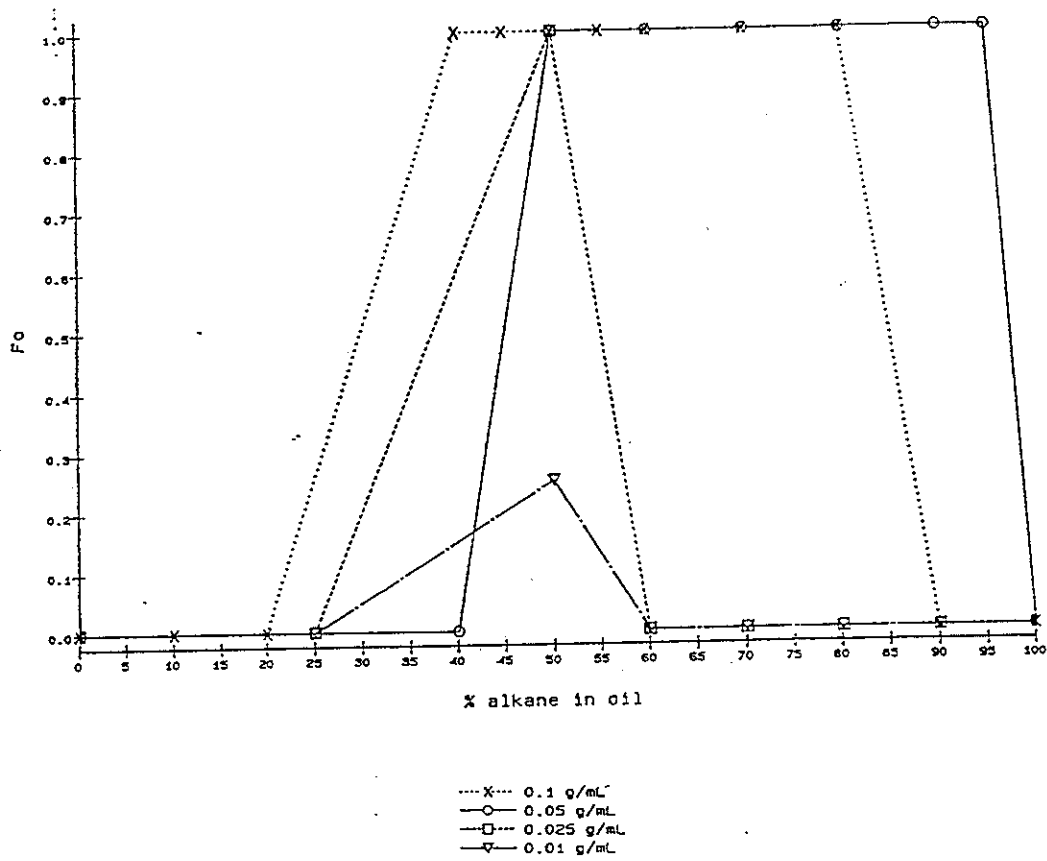


Figure 10: F_{final} versus % alkane

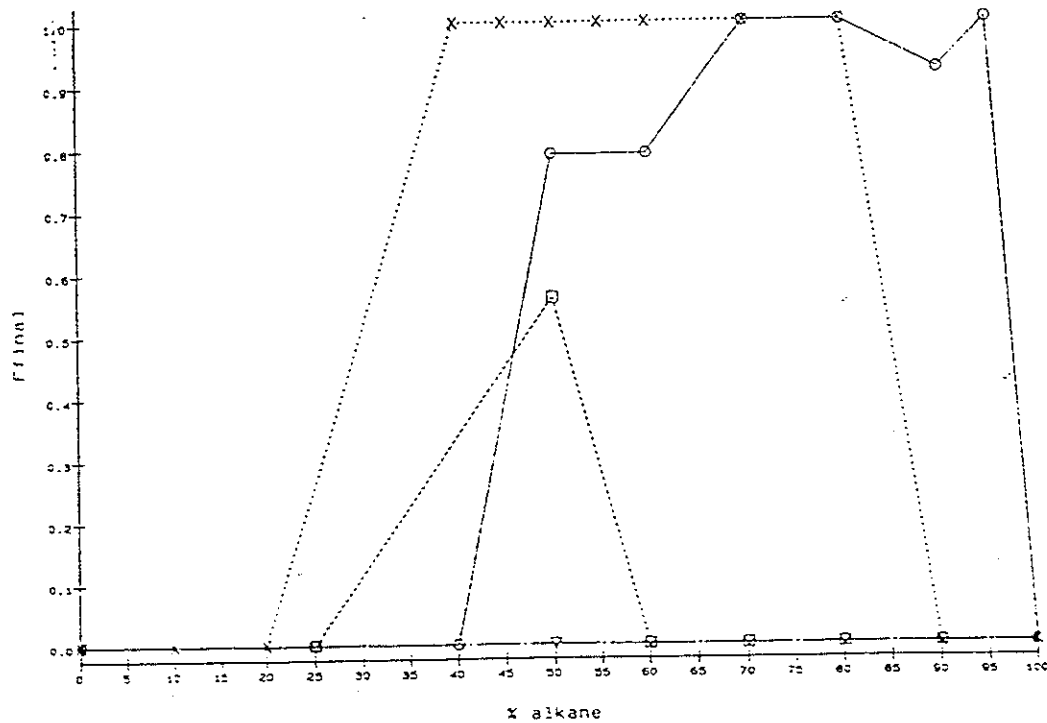


Figure 11: Water content vs % alkane

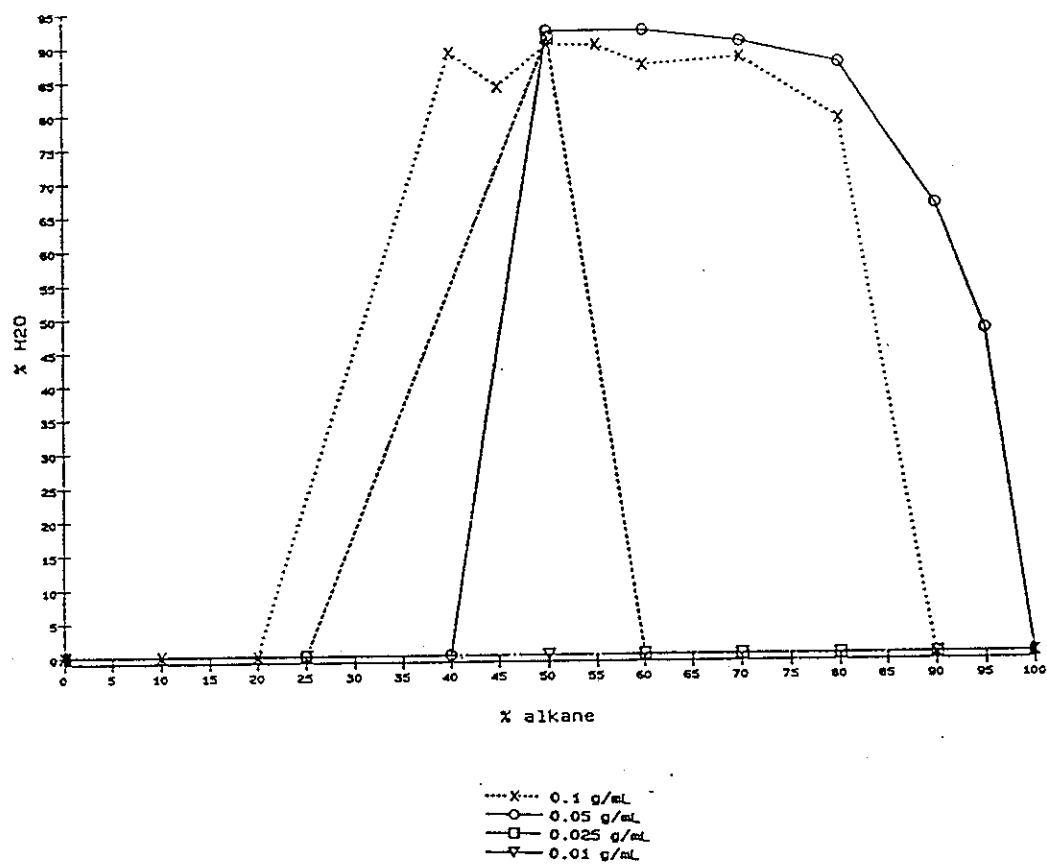


Figure 12: Yield point vs % alkanes

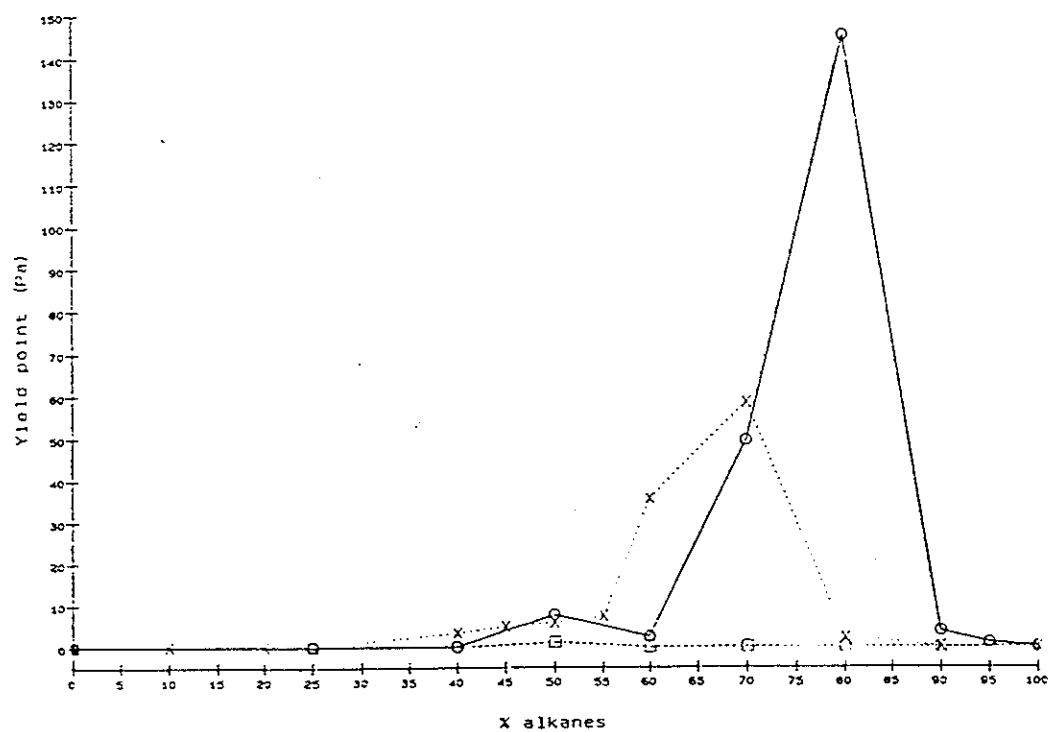
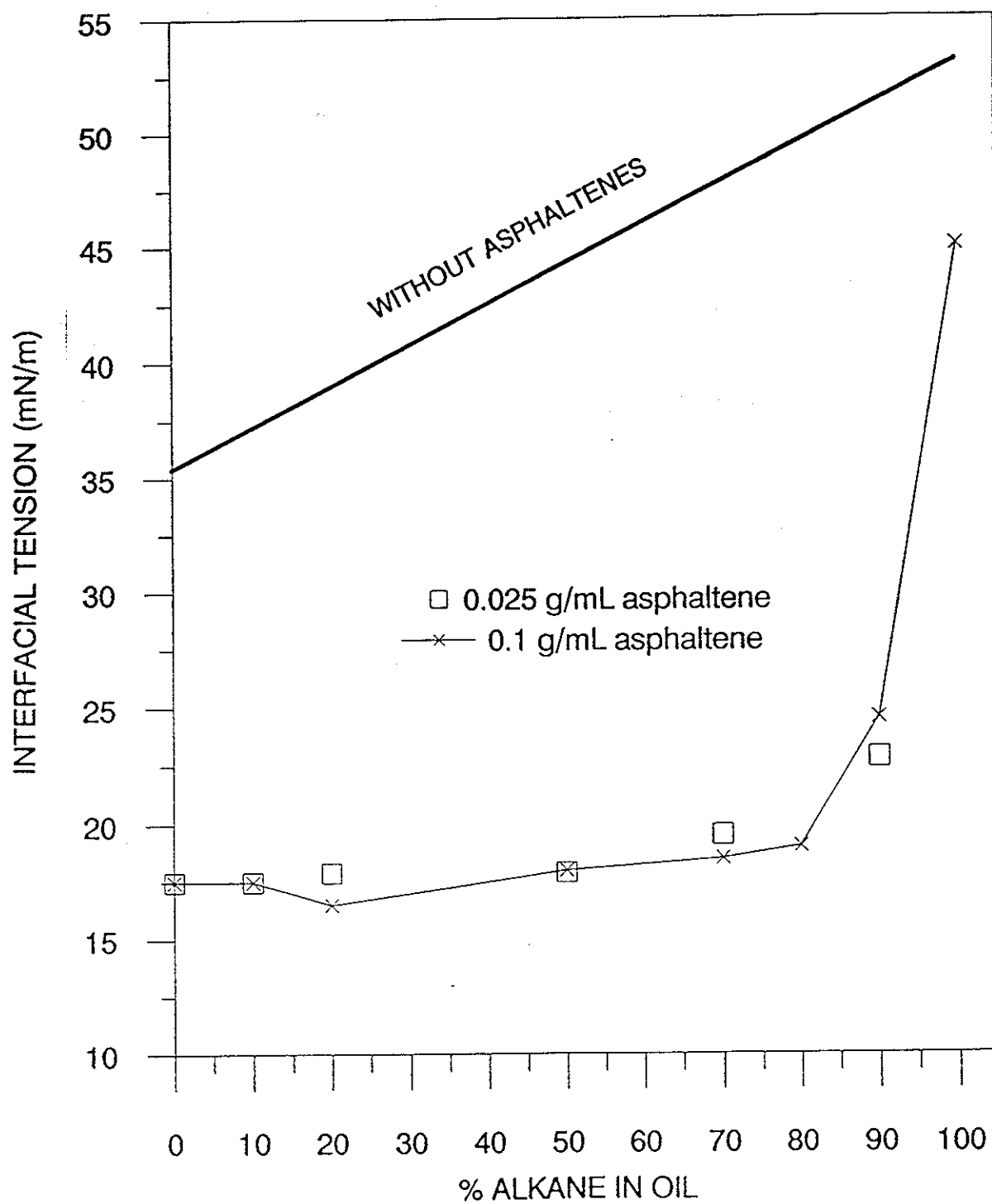


Figure 13: Effect of asphaltene concentration on oil/water interfacial tension.



Comparison of Asphaltenes from Different Crudes

Asphaltenes from different oils will differ in elemental composition, structure and molecular weight. Therefore, the solubility/precipitation behaviour of asphaltenes from different sources could potentially differ. The experiments using the heavy paraffin oil/xylene oil containing 0.05 g/mL asphaltenes were repeated for asphaltenes extracted from Prudhoe Bay crude oil, Figure 14 to 17. Overall, the emulsification behaviour was very similar to the California crude asphaltenes. The asphaltenes from the California crude were slightly more effective emulsifiers.

Figure 14: F_o versus % alkane for oils with asphaltenes from Prudhoe Bay Crude oil.

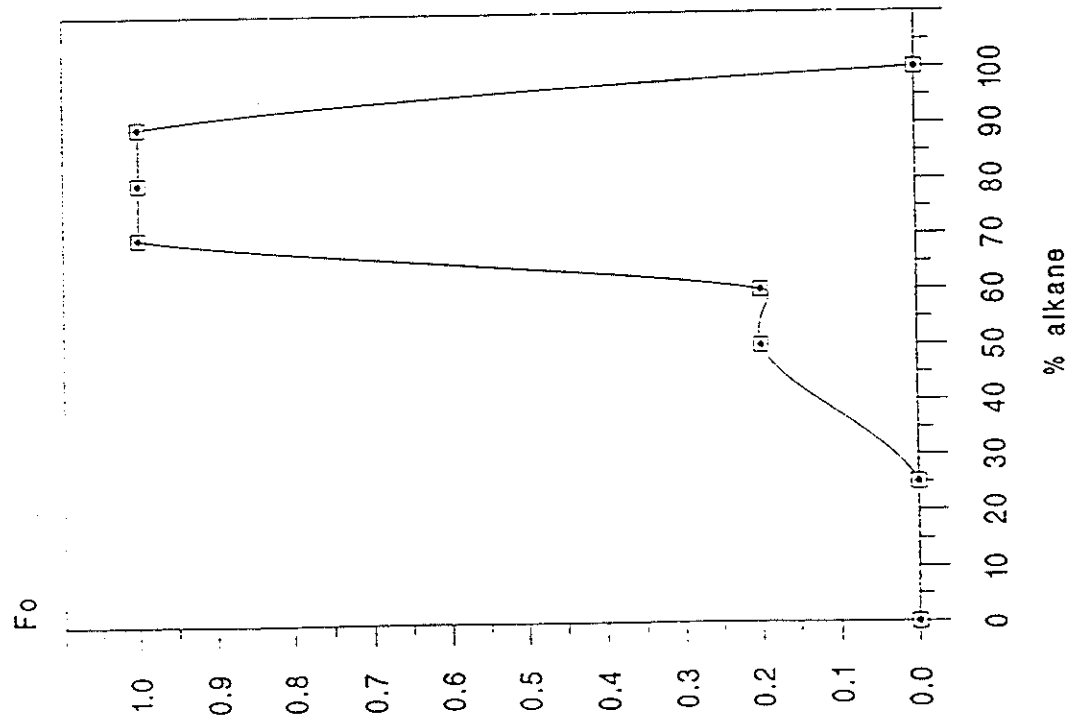


Figure 15: F_{final} versus % alkane.

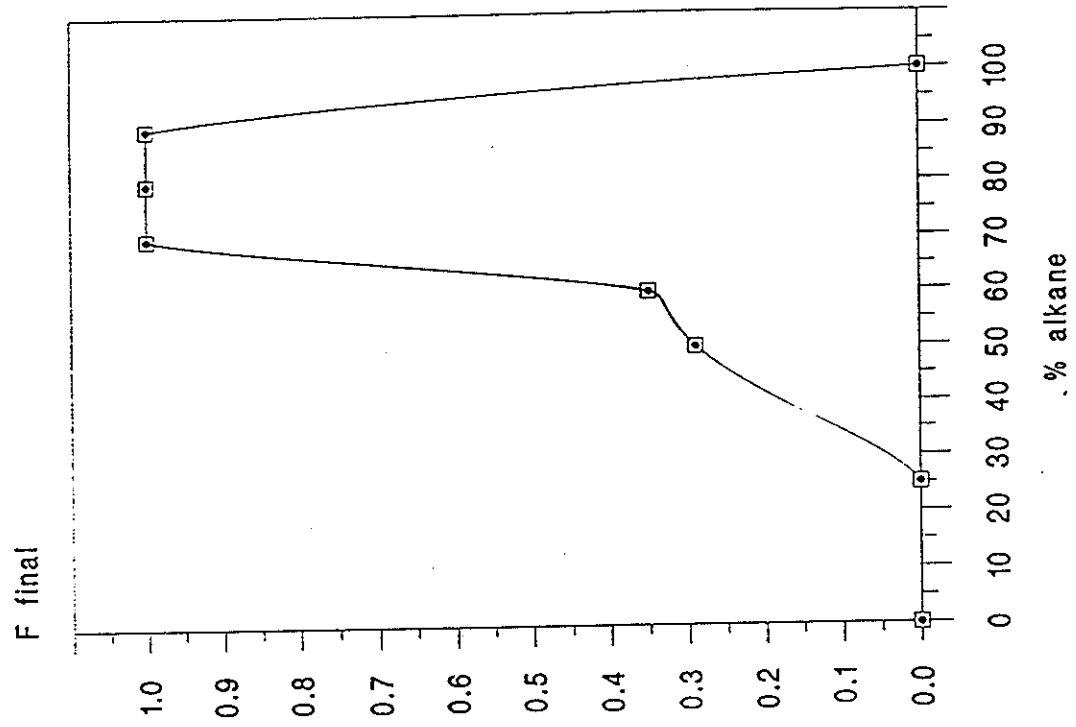


Figure 16: Water content versus % alkane.

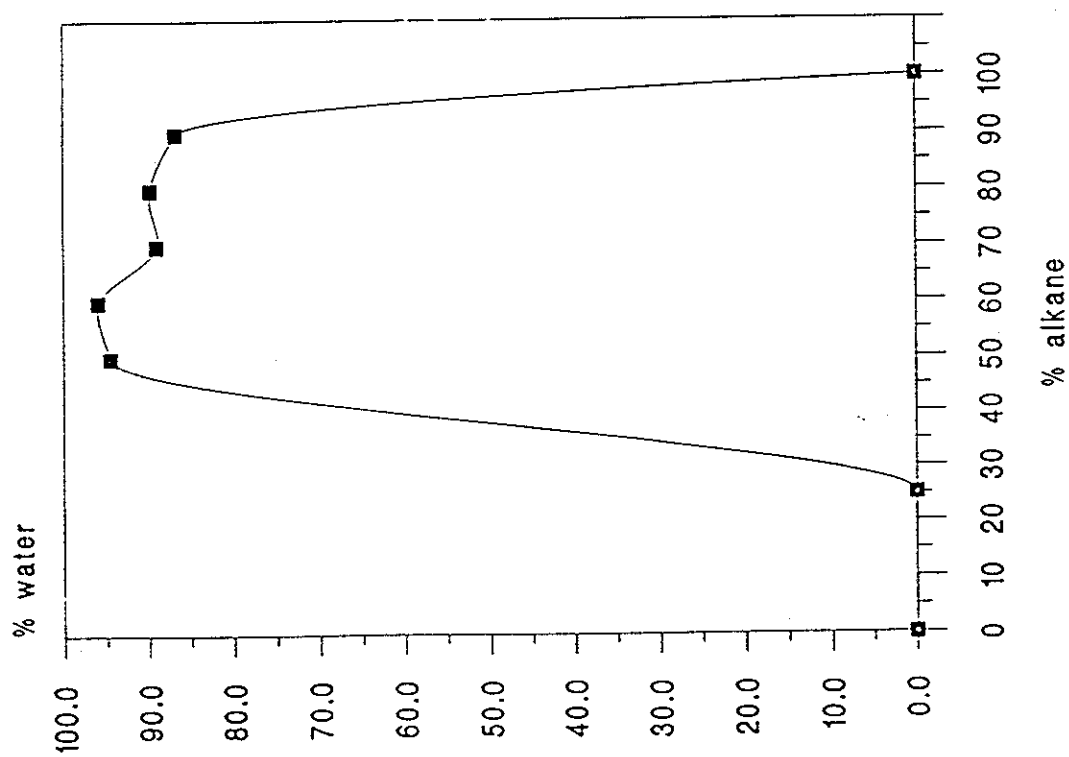
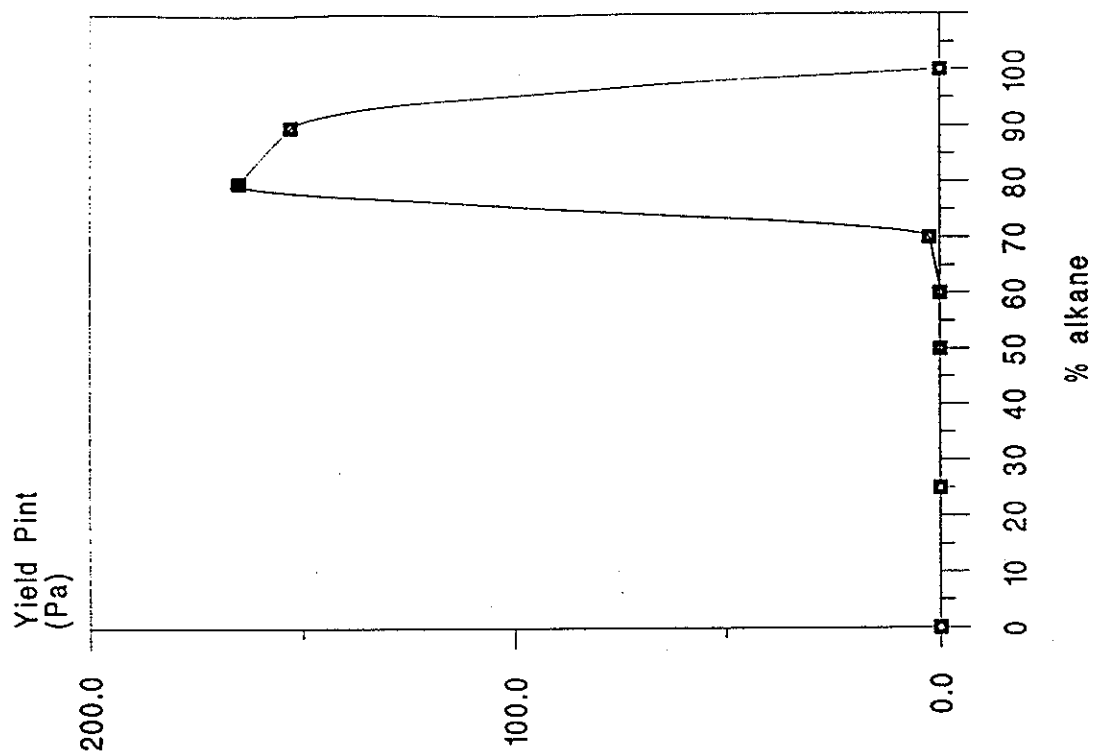


Figure 17: Yield point versus % alkane.



Effect of Changing Alkane and Aromatic Components

From the Hildebrand-Scatchard equation, it can be seen that the amount of asphaltenes soluble in oil, X_a , is controlled by the term $(\delta_a - \delta_s)^2$. As $(\delta_a - \delta_s)^2$ increases, the amount of asphaltenes soluble in oil decreases, and any excess asphaltenes precipitates. Therefore, the probability of producing a stable emulsion should correlate with the value of $(\delta_a - \delta_s)^2$. In Figure 18, F_{Final} values are plotted as a function of $(\delta_a - \delta_s)^2$ for eight model oils containing different alkane and aromatic components. It can be seen that stable emulsions only form when $(\delta_a - \delta_s)^2$ has a value of approximately 60 MPa or greater. Note that data on the graph does not include points where the model oils are 100% alkane. As previously mentioned, it is an artifact of the method used to prepare the oils that prevents these oils from forming emulsions.

Solubility parameters can either be measured experimentally or calculated using compositional data. For the model oils, the solvency strength is determined by the alkane and aromatic composition. For aromatic compounds, the value of the solubility parameter decreases as the molecular weight is increased along a homologous series. Therefore, asphaltenes will be less soluble in model oils as the solubility parameter of the aromatic component is decreased. Results from experiments where different aromatic solvents were used as the aromatic component for the model oil showed that as the solubility parameter of the aromatic solvent decreased, the oil would form stable emulsions over a larger range of alkane/aromatic ratios. Figures 19 to 22 show F_o , F_f , water content, and yield point versus percent alkane for five different model oils consisting of heavy paraffin oil, 0.05 g/mL asphaltenes, and five different aromatic solvents. These being xylene; phenyl octane (PO); dimethyl naphthalene (DMN); diphenyl methane (DPM); and an equal volume mixture of the four solvents (MIX). As the results illustrate the aromatic component has a profound effect upon the emulsification behaviour of the oil. This can be best explained in terms of the Hildebrand solubility parameter, σ (units: $\text{MPa}^{1/2}$). The values for these parameters are 24.7 for the asphaltenes; 15.0 for heavy paraffin oil; 18.0 for xylene; 17.5 for phenyl octane; 21.0 for dimethyl naphthalene; 19.5 for diphenylmethane; and 19.0 for the mixture.

Figure 18: F_{Final} as a function of $(\delta_a - \delta_s)^2$ for eight model oils containing different alkane and aromatic components.

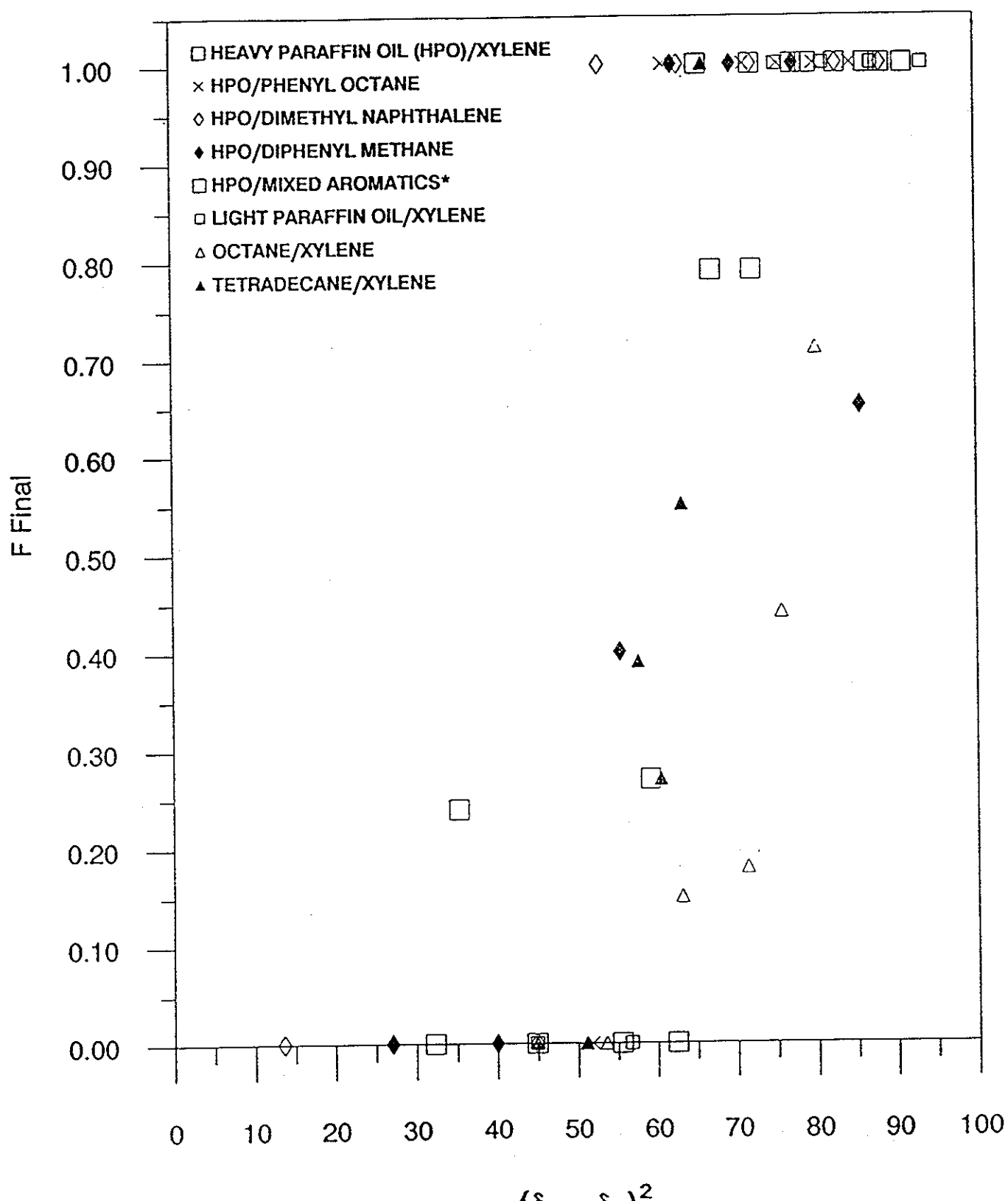


Figure 19: F_0 vs % alkane
different aromatic components

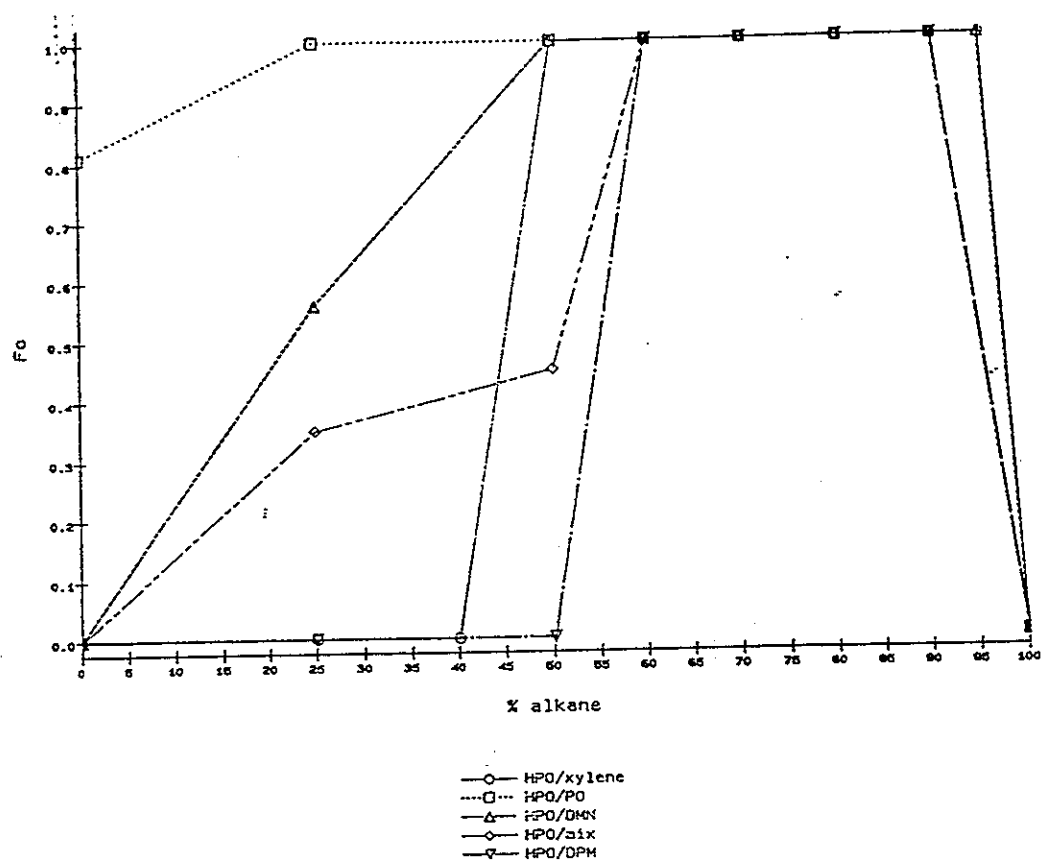


Figure 20: F_{final} vs % alkane

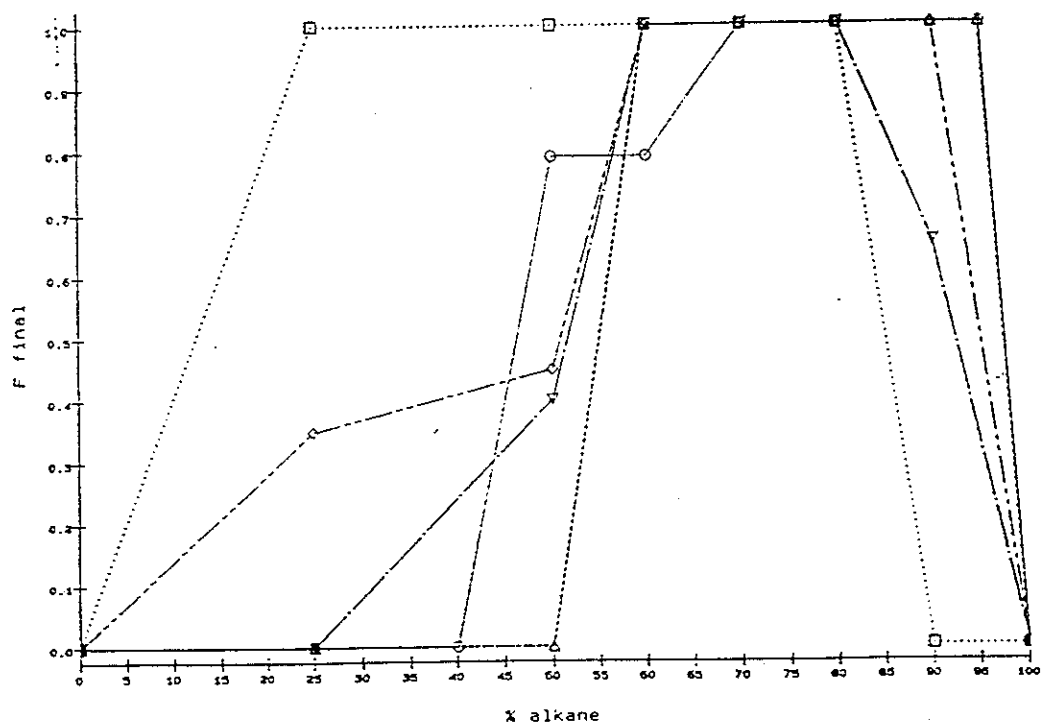


Figure 21: Water content vs % alkane

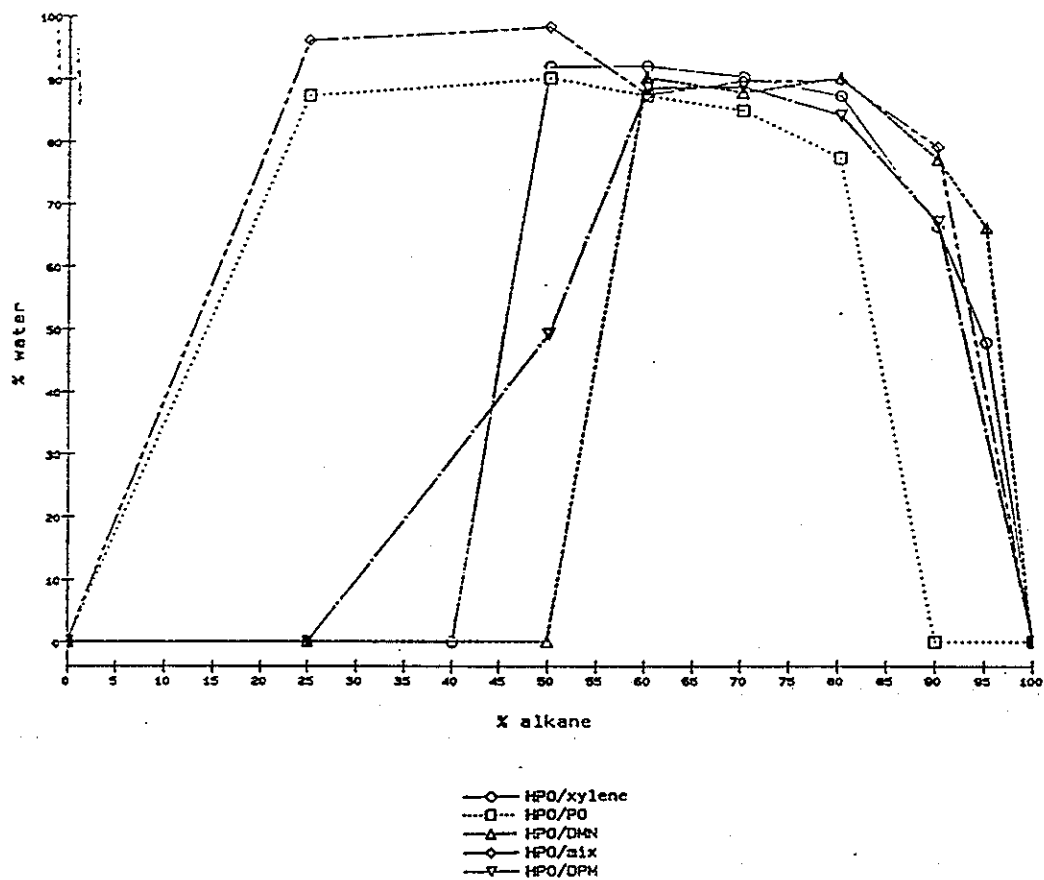
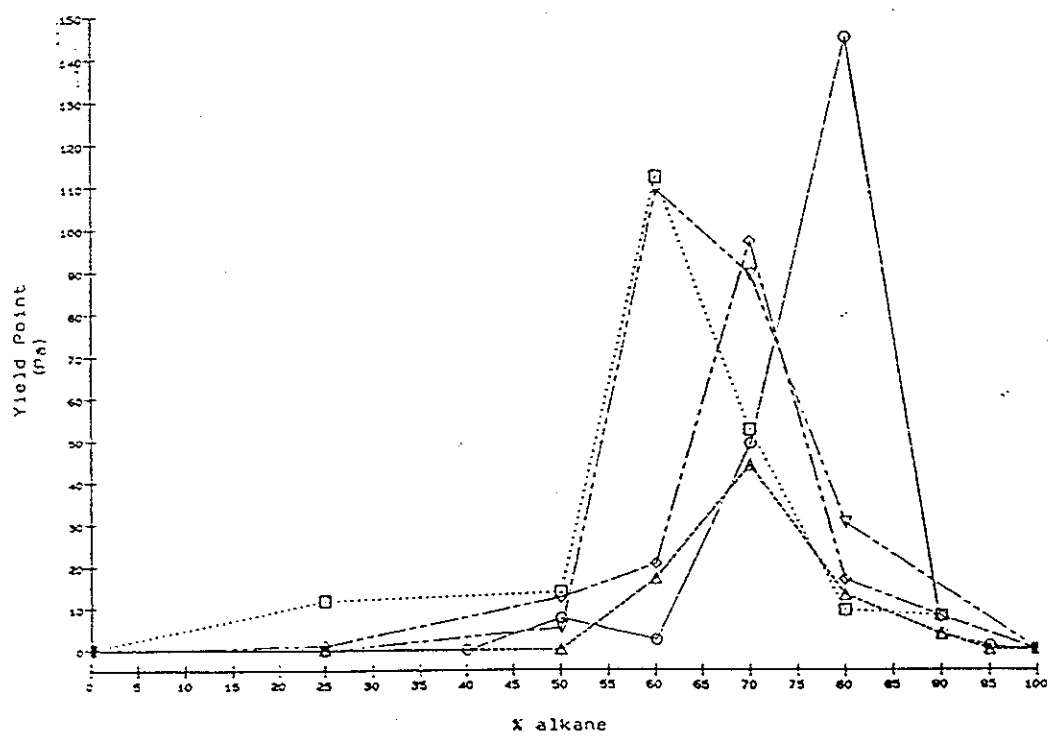


Figure 22: Yield point vs % alkane



The effect of using different alkane solvents as the precipitation medium for asphaltenes has been studied by Long (Long 1979), Speight and Moschopedis (Speight and Moschopedis 1979). Their findings indicate that as the carbon number of the alkane solvent increases, the amount of asphaltenes which precipitate decreases, and that the composition of the precipitated material also changes. Higher alkane solvents were shown to yield asphaltenes which have a higher degree of aromaticity, a higher proportion of heteroatoms, a higher degree of polarity, and higher molecular weights. Results from this study indicate that the model oils have a stronger tendency to form stable emulsions as the molecular weight of the alkane component increases and if the component is a mixture of alkanes (i.e. the paraffin oils) rather than a single alkane solvent.

Figures 23 to 26 show F_o , F_f , water content, and yield point versus percent alkane for four different model oils consisting of xylene, 5% asphaltenes, and four different alkane components: n-octane ($\sigma = 15.4$), n-tetradecane ($\sigma = 16.3$), light paraffin oil ($\sigma = 14.7$), and heavy paraffin oil ($\sigma = 15.0$). The results show that the model oils containing the paraffin oils (a complex mixture of alkanes) have a stronger tendency to form stable emulsions than do the oils made with the n-alkane solvents. The emulsions formed by oil containing the heavy paraffin oil are structurally stronger (higher yield points) than those formed by the light paraffin oil. When the emulsification behaviour of the model oils containing octane and tetradecane are compared, the tetradecane/xylene oil has a stronger tendency to form stable emulsions (higher F_f values), but these emulsions have less structural strength (lower yield point).

Figure 23: F_0 versus % alkane
for different alkane components

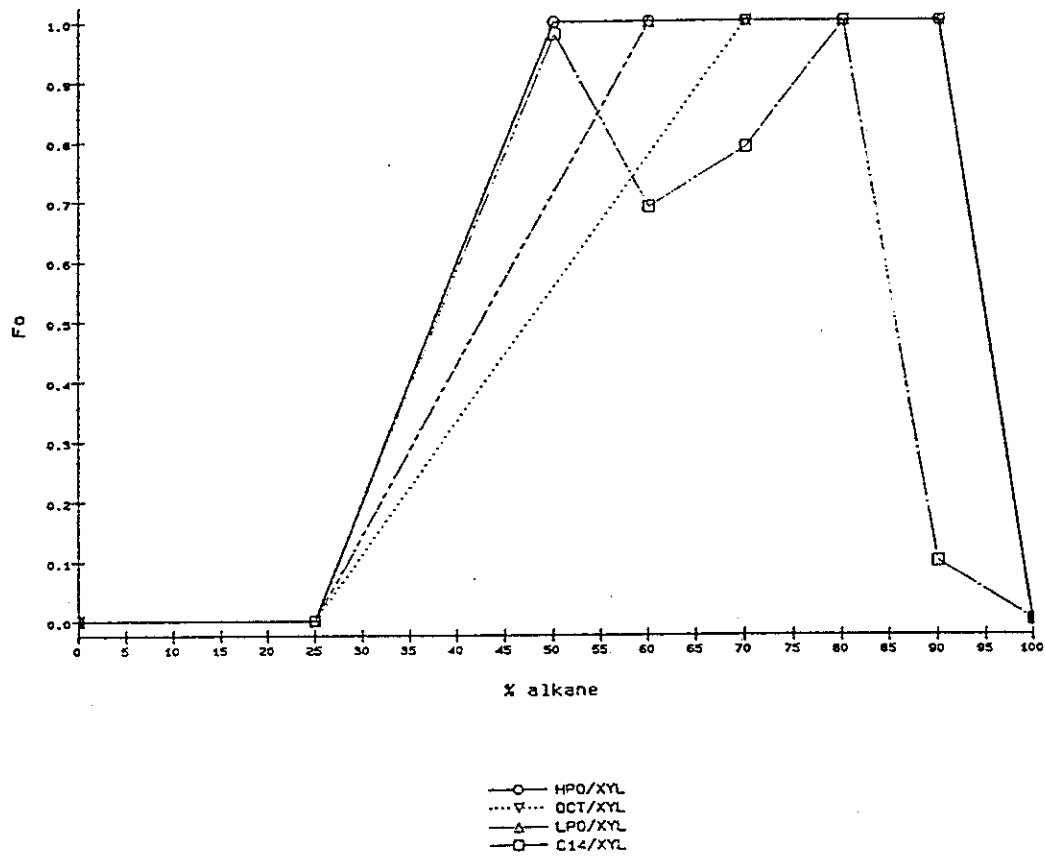


Figure 24: F_{final} vs % alkane

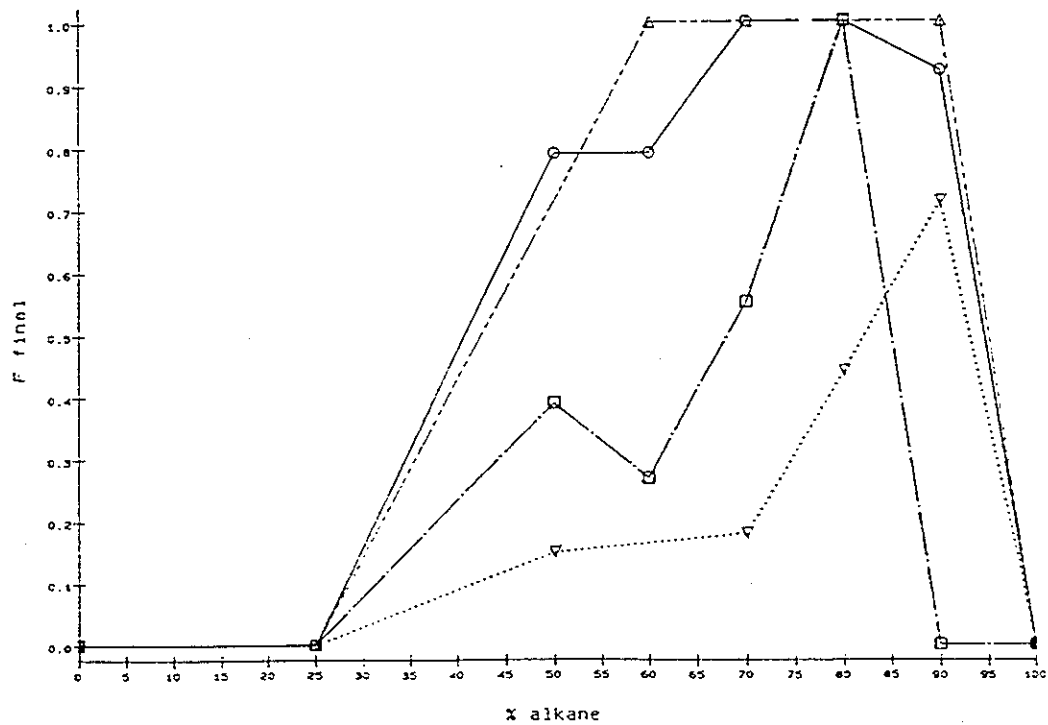


Figure 25: Water content vs % alkane

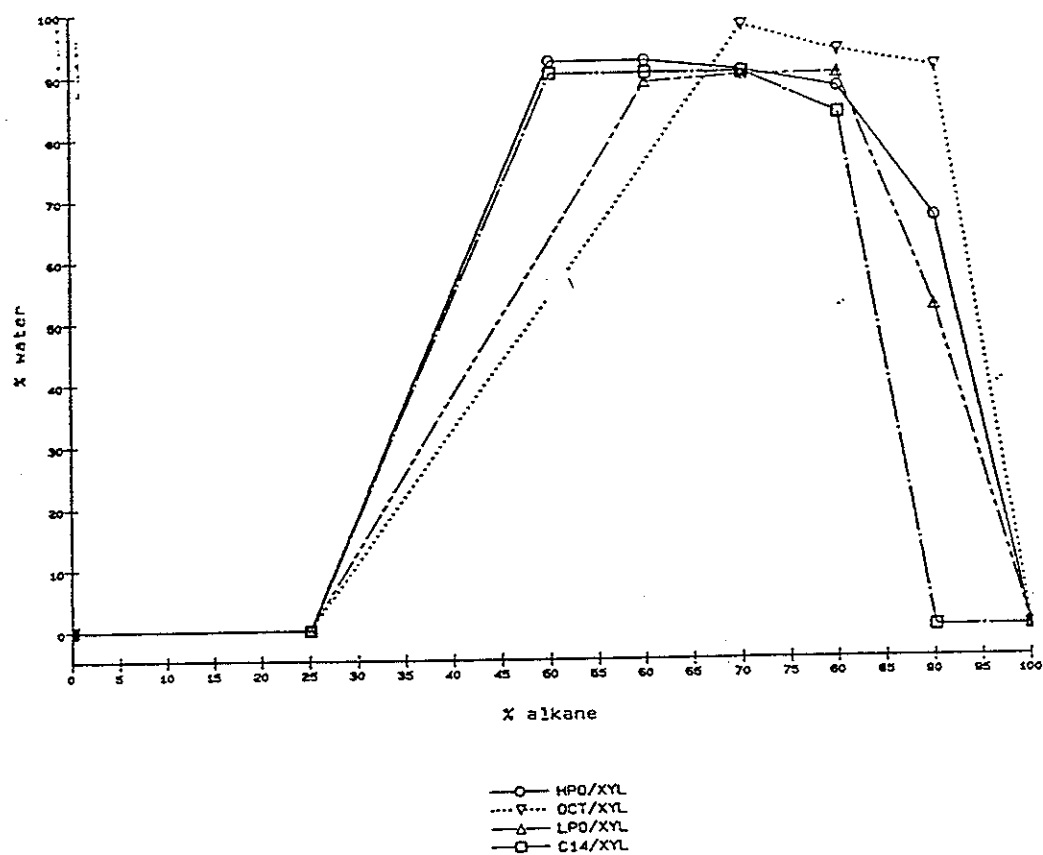
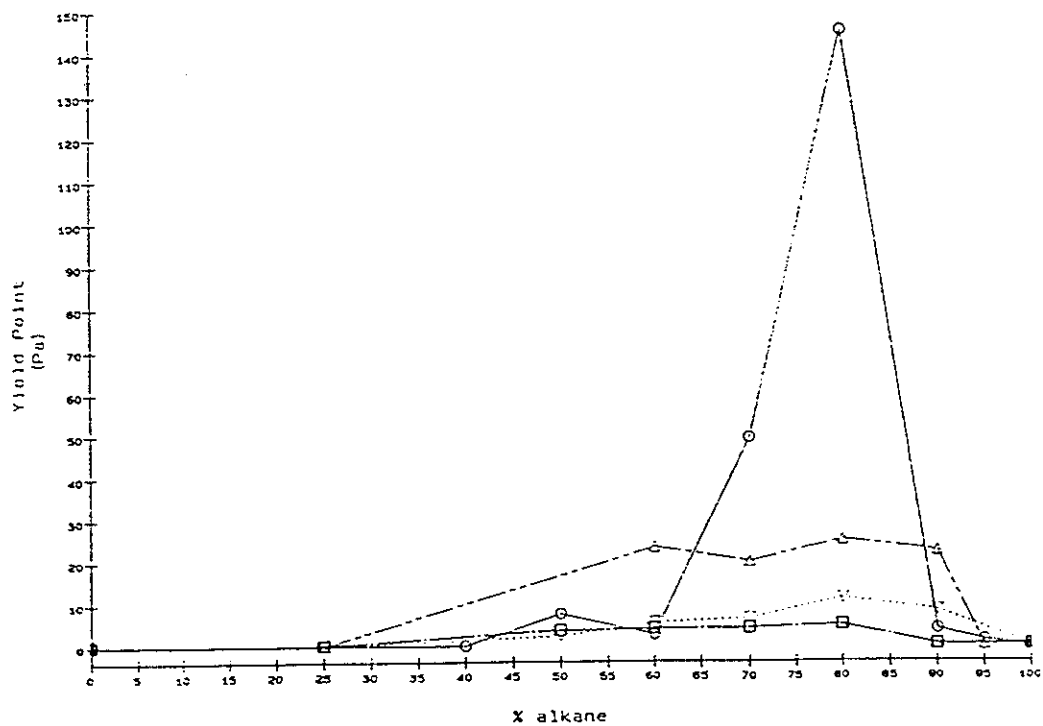


Figure 26: Yield Point vs % alkane



To date, no study has examined either the change in solvency or the precipitation of asphaltenes as a function of oil weathering. But undoubtedly the rapid loss of C_{10} and lighter hydrocarbons from oil within hours of a spill (McAuliffe 1989) has a dramatic effect upon solvency and phase equilibrium. Results from this study indicate that the compositional changes which occur as a result of oil weathering, would strongly favour the precipitation of asphaltenes. It is speculated that spilled oil rapidly emulsifies into stable mousse once this precipitation is initiated. It is known that weathered oil has a greater tendency to form mousse than fresh oil, but this has largely been attributed to the physical changes which are induced by weathering. Indeed, weathering causes an increase in oil density and viscosity, and concentrates the indigenous emulsifiers in the remaining oil. All of these changes would enhance the formation of water-in-oil emulsions (Becher 1983).

Resins as Emulsifying Agents

Figures 27 to 30 present the emulsification behaviour for model oils where the emulsifying agents are: 1. asphaltenes; 2. resins; and 3. asphaltenes and resins together. The results show that resins alone can act as effective emulsifiers. The range of alkane/aromatic ratios over which stable emulsions are produced is smaller than for asphaltene-containing oils. When asphaltenes and resins are both present, the range over which stable emulsions are formed is larger than either resins or asphaltenes alone.

Figure 27: F_0 versus % alkane
effect of resins

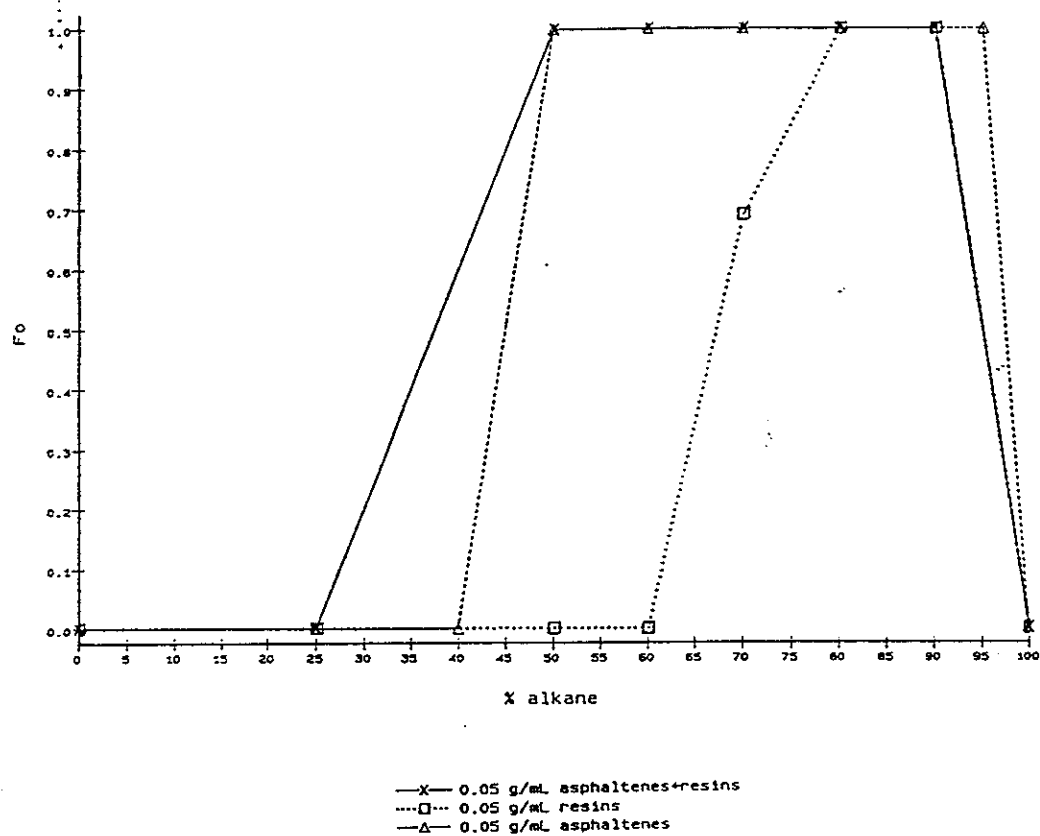


Figure 28: F_{final} vs % alkane

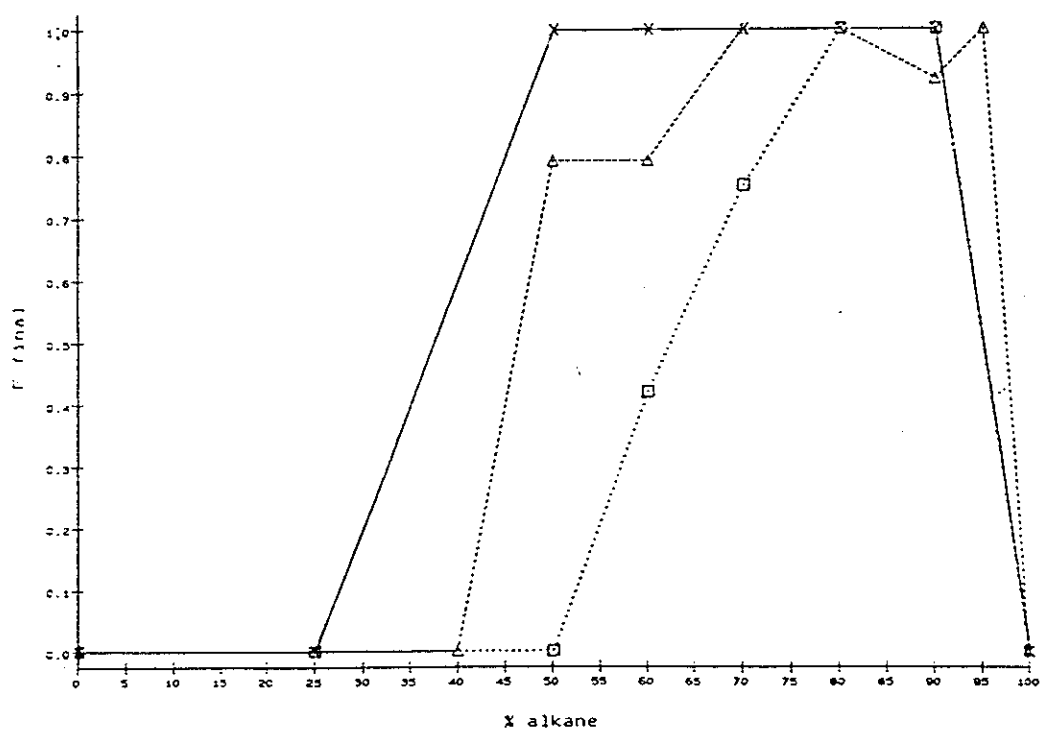


Figure 29: Water content vs % alkane

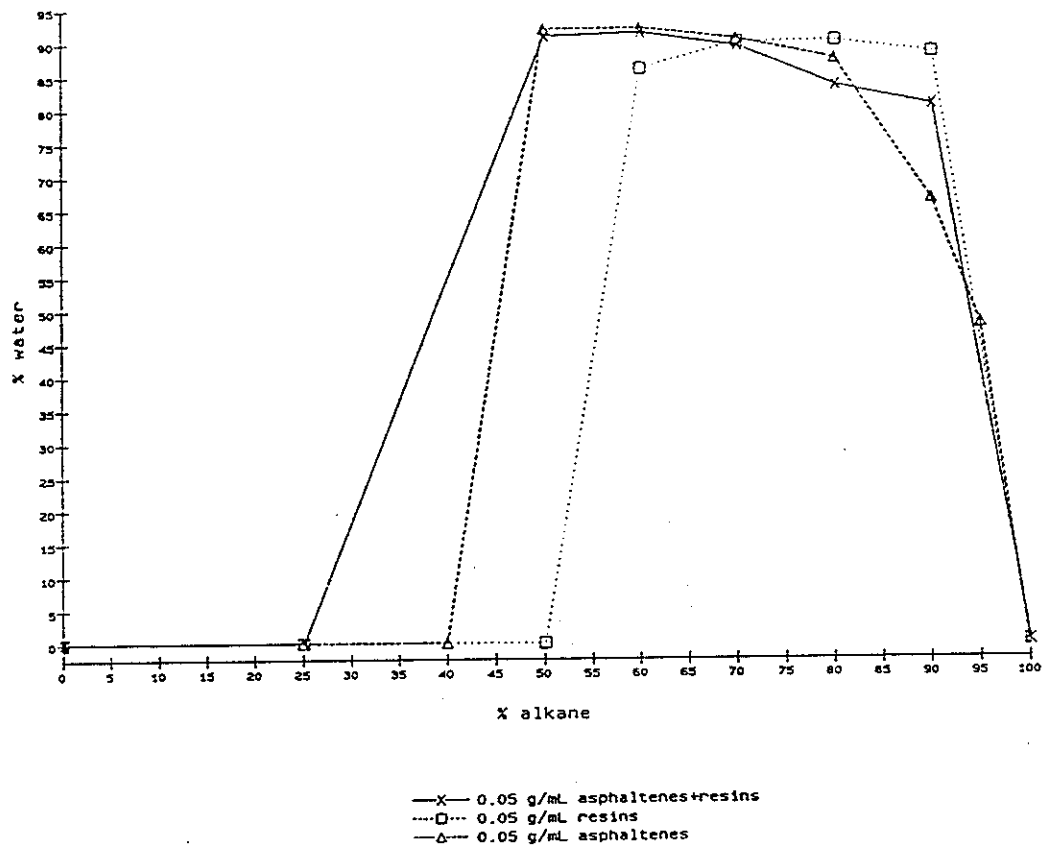
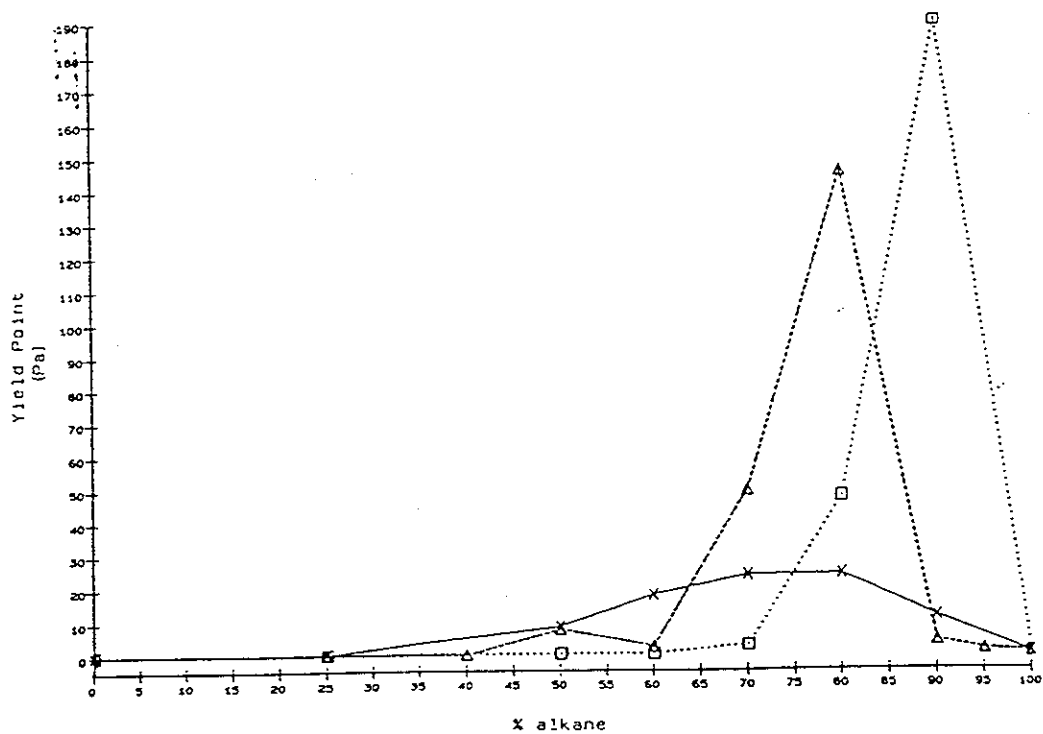


Figure 30: Yield Point vs % alkane



Waxes as Emulsifying Agents

Model oils containing only waxes as the emulsifying agent had no tendency to emulsify. Figure 31 to 34 shows the effect of adding 0.05 and 0.1 g/mL of wax to a model oil containing 0.01 g/mL of asphaltenes. The oil containing 0.01 g/mL of asphaltenes had no tendency to form stable emulsions but the addition of wax clearly increases the tendency of the oil to form stable emulsions at nearly all alkane/aromatic ratios. As the concentration of wax is increased, the oil has a greater tendency to produce stable emulsions.

The effect of adding 0.1 g/mL of wax to the model oil containing 0.05 g/mL asphaltenes is shown in Figures 35 to 38. The addition of wax has little effect upon F_o , F_f and water content but decreases the yield point of the emulsions formed.

Figures 39 to 42 show the effect of increasing asphaltene content upon an oil containing 0.05 g/mL grams of wax. Model oils containing only wax as the emulsifying agent had no tendency to emulsify. As the Figures illustrate, the addition of asphaltenes results in the formation of stable emulsions. As the concentration of asphaltenes is increased, the oils have a greater tendency to produce stable emulsions.

Waxes are too hydrophobic to make sufficient contact with the interface to act as emulsifying agents by themselves. However, the waxes can interact with the asphaltenes in such a way that precipitated wax is able to stabilize the emulsion. It is estimated that when waxes constitute the majority of particles present in these oils, a minimum particulate concentration of around 0.06 g/mL must exist in the oil and that 0.01 g/mL of these particles must be asphaltenes.

Figure 31: F_0 vs % alkane
effect of increasing wax content

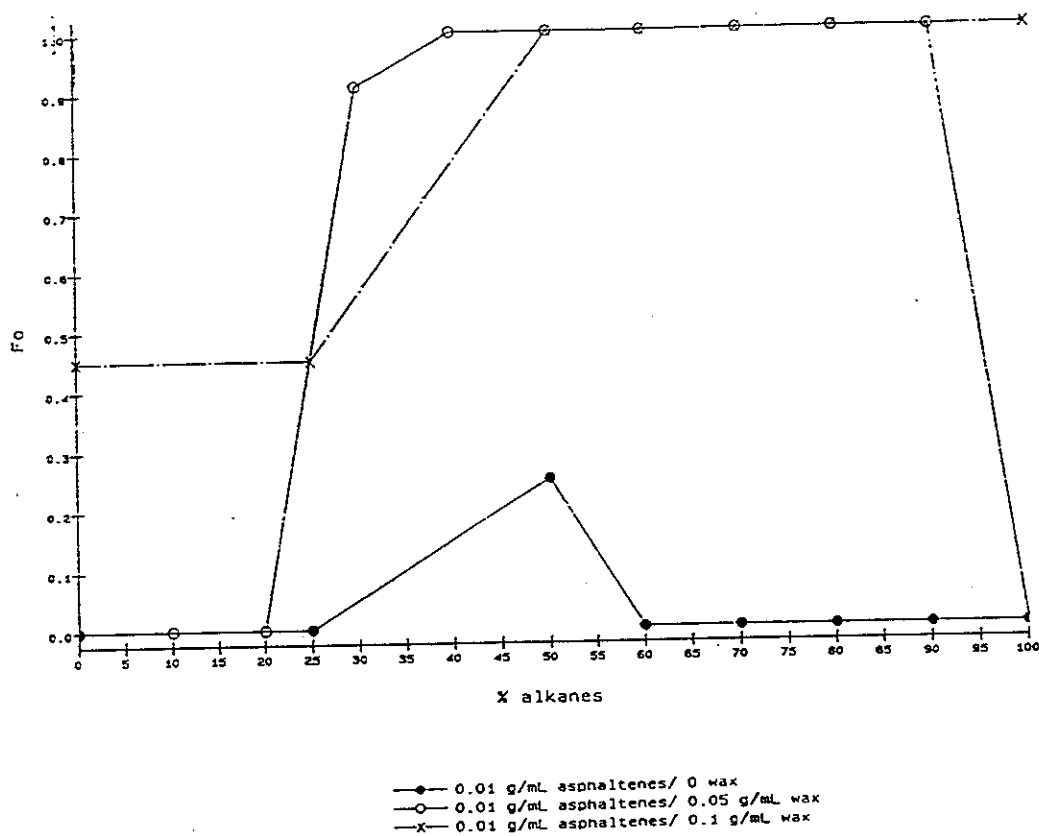


Figure 32: F_{final} vs % alkane

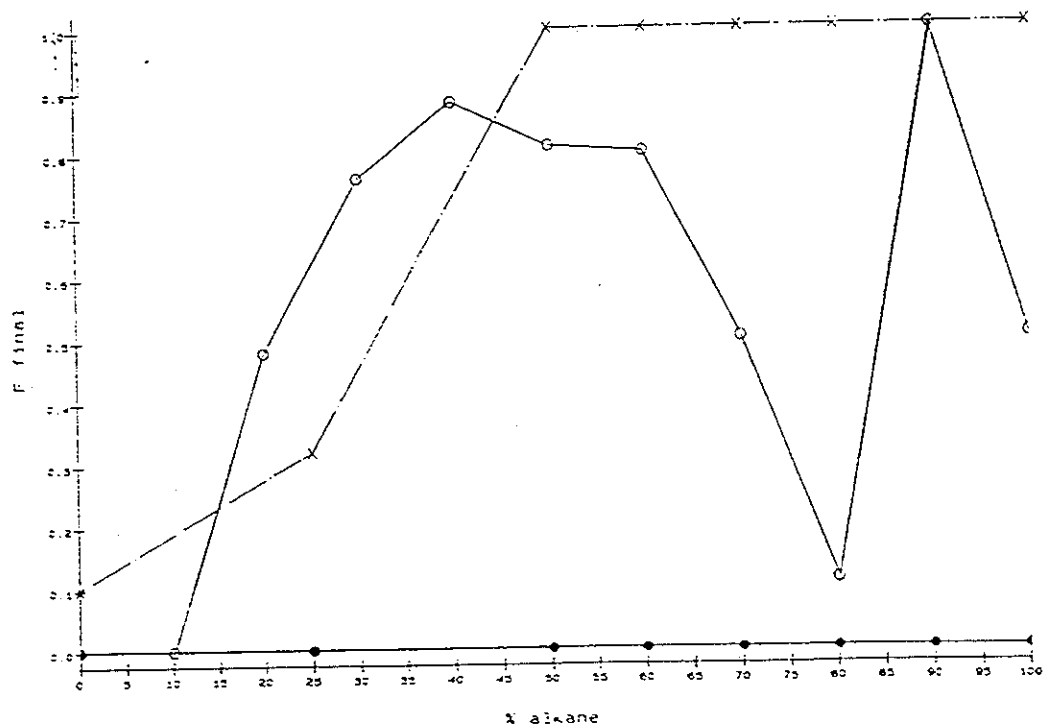


Figure 33: Water content vs % alkane

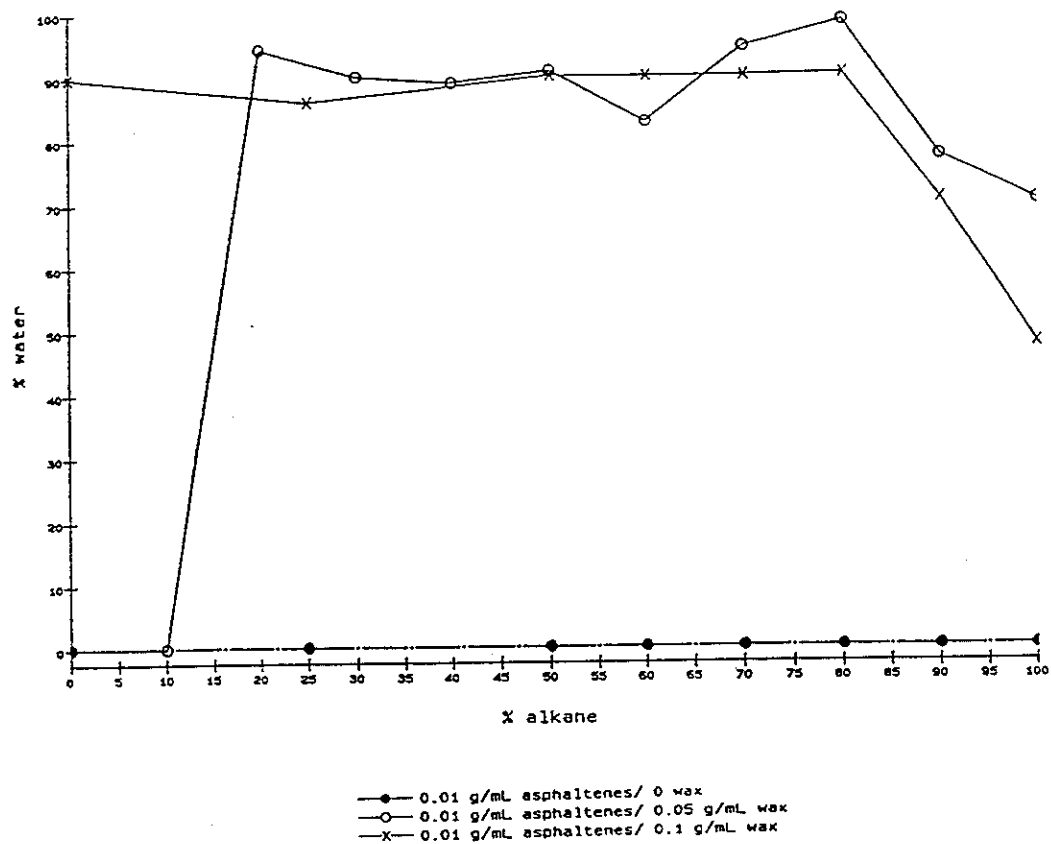


Figure 34: Yield Point vs % alkane

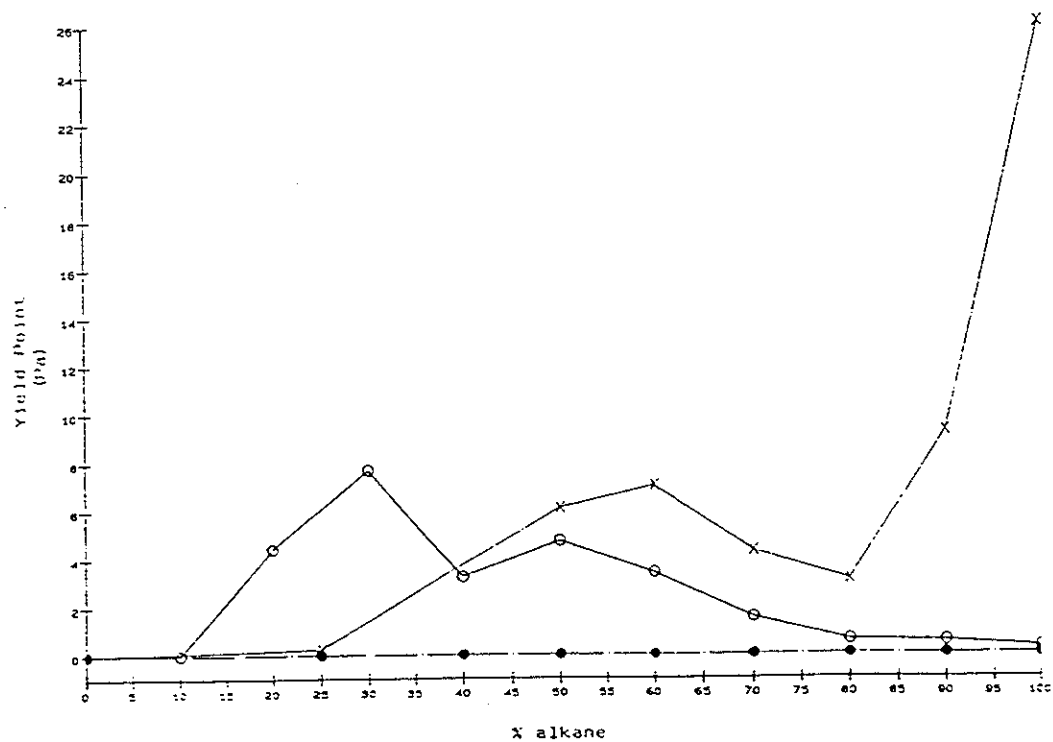
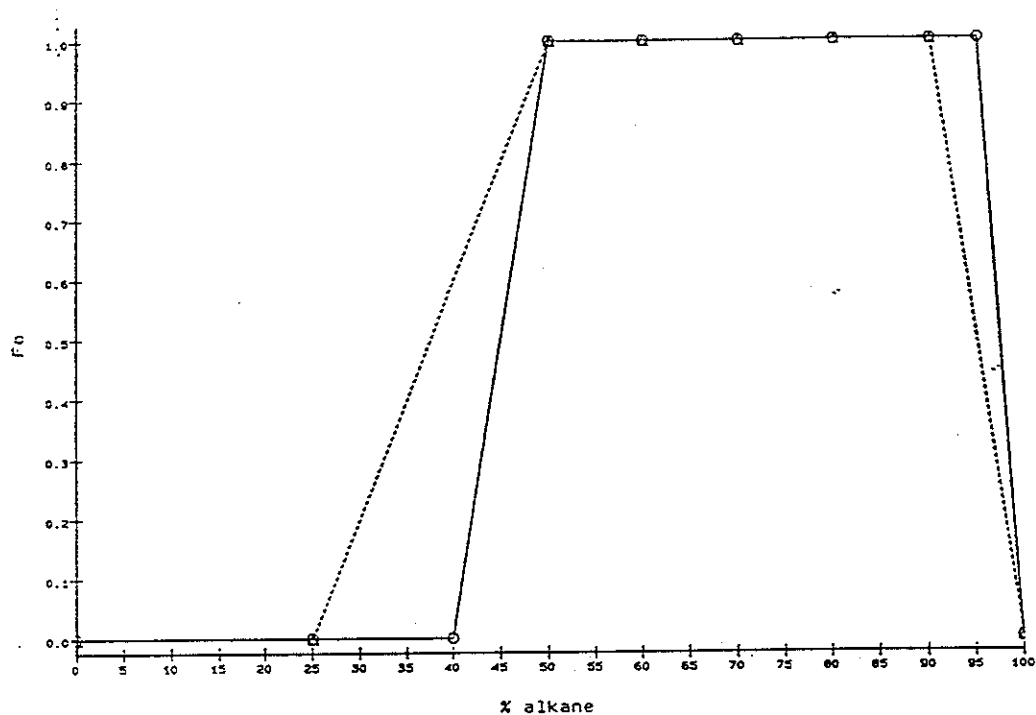


Figure 35: F_0 versus % alkane
effect of adding wax



—○— 0.05 g/mL asphaltene / 0 wax
- -△- - 0.05 g/mL asphaltene / 0.1 g/mL wax

Figure 36: F_{final} vs % alkane

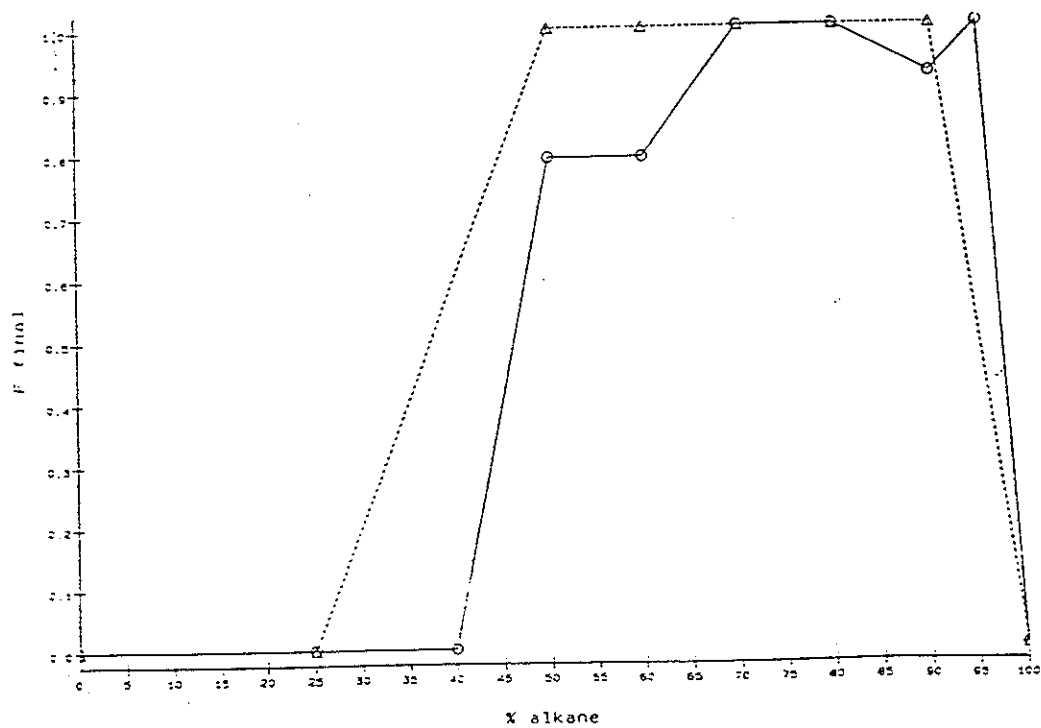


Figure 37: water content vs % alkane

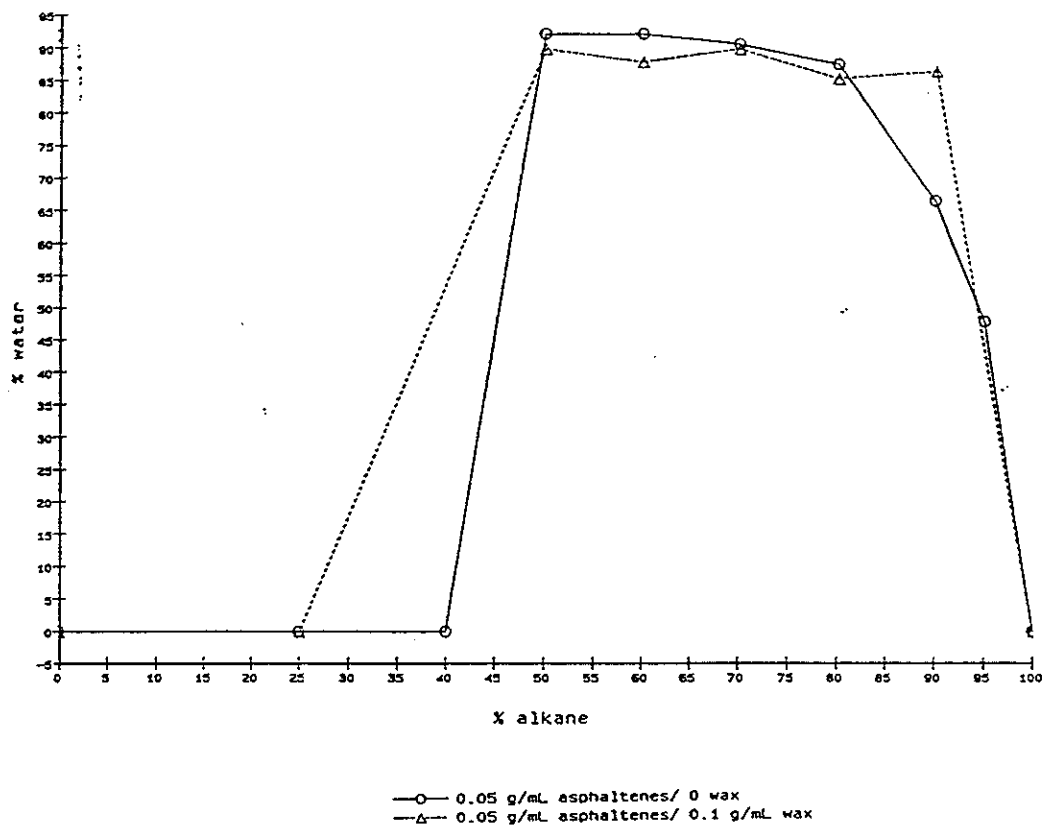


Figure 38: Yield point vs % alkane

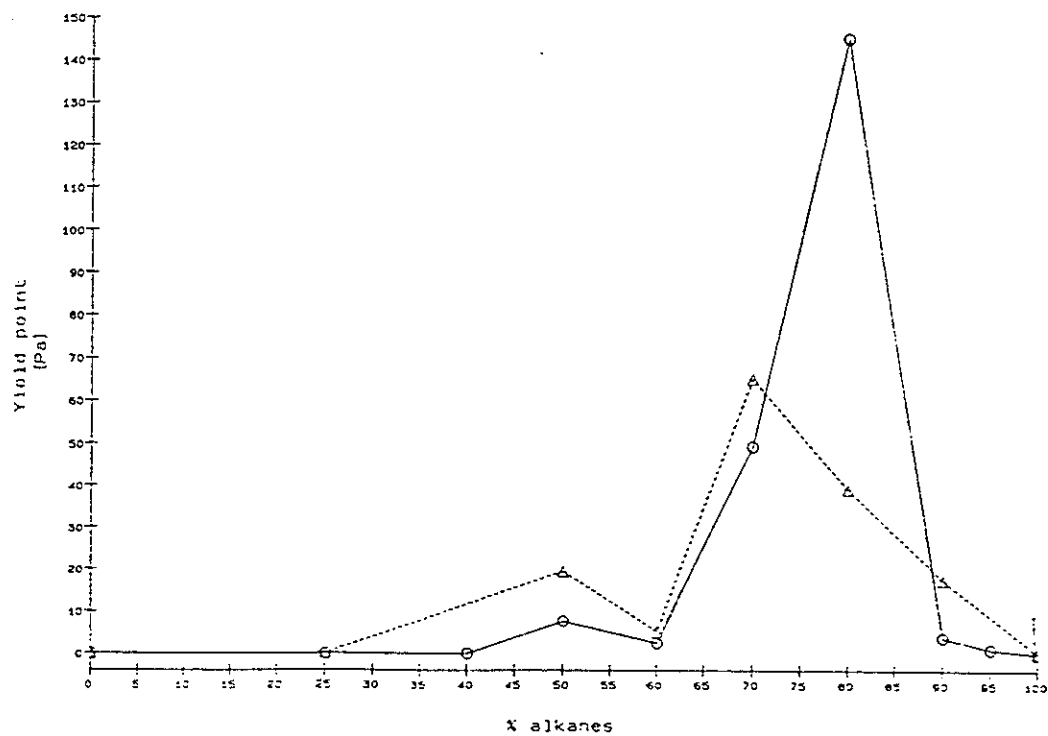


Figure 39: F_o versus % alkane
effect of increasing asphaltene concentration
in an oil having a wax concentration of 0.05 g/mL

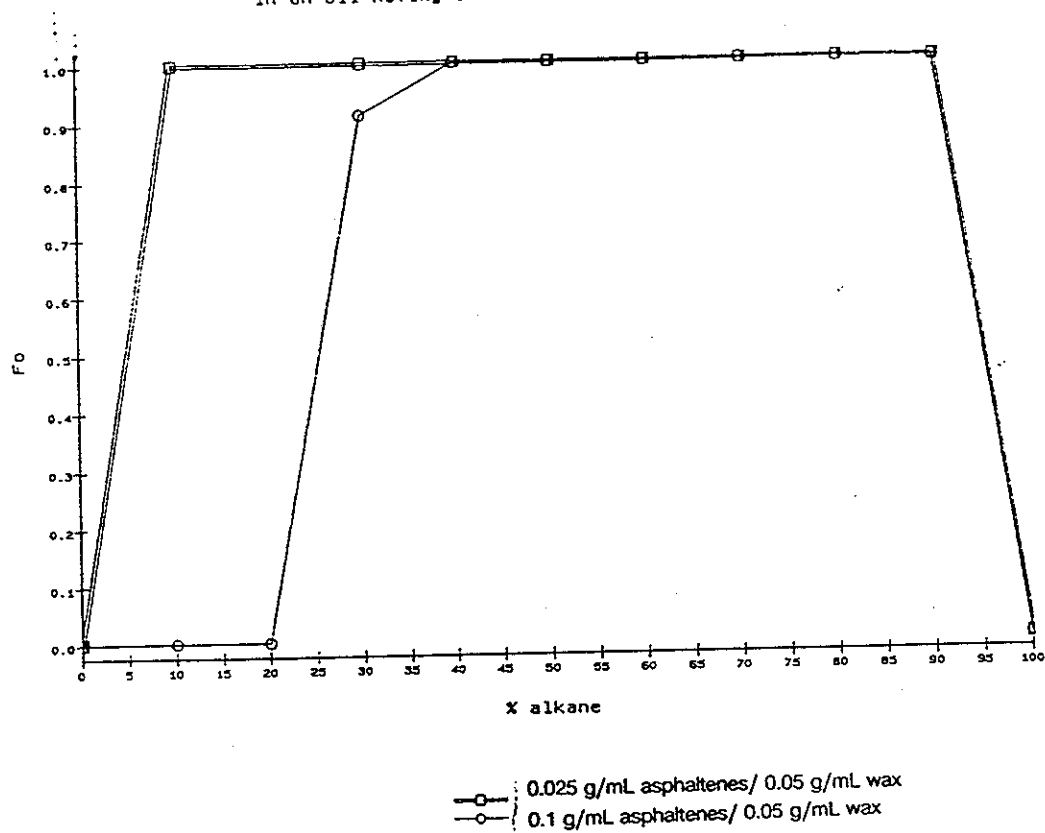


Figure 40: F_{final} vs % alkane

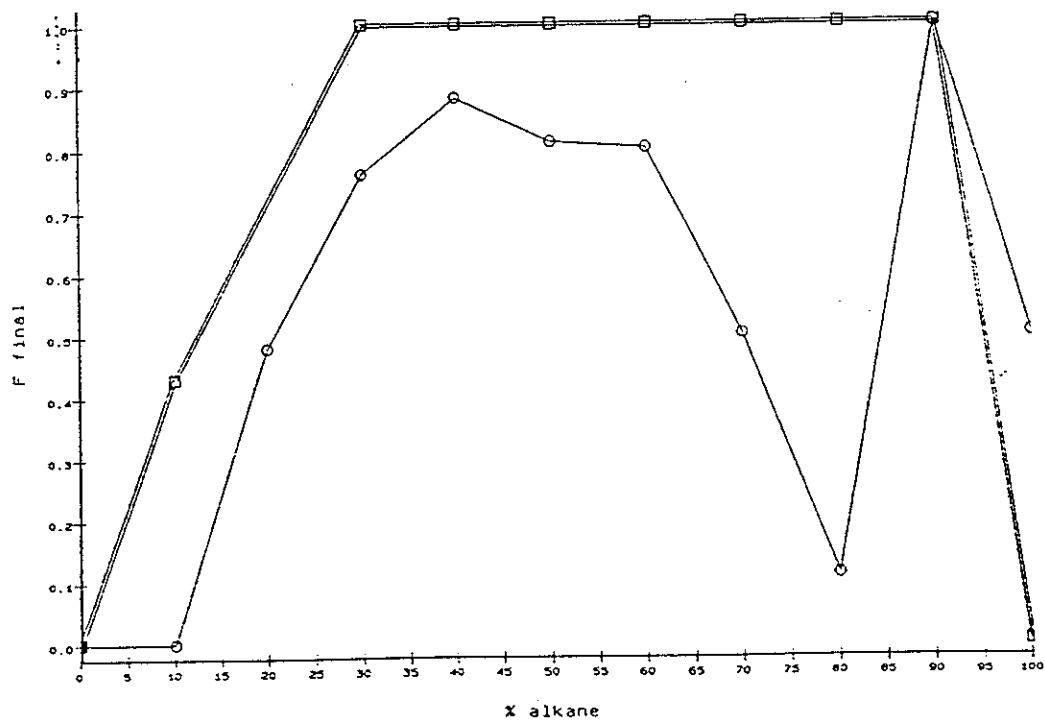
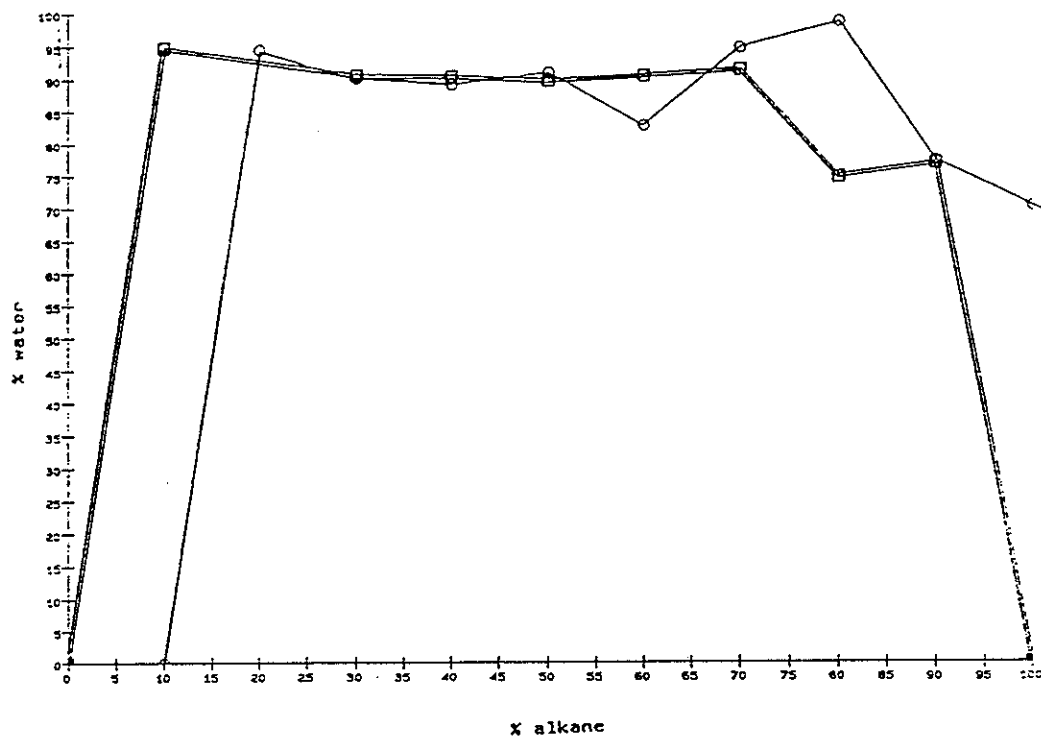
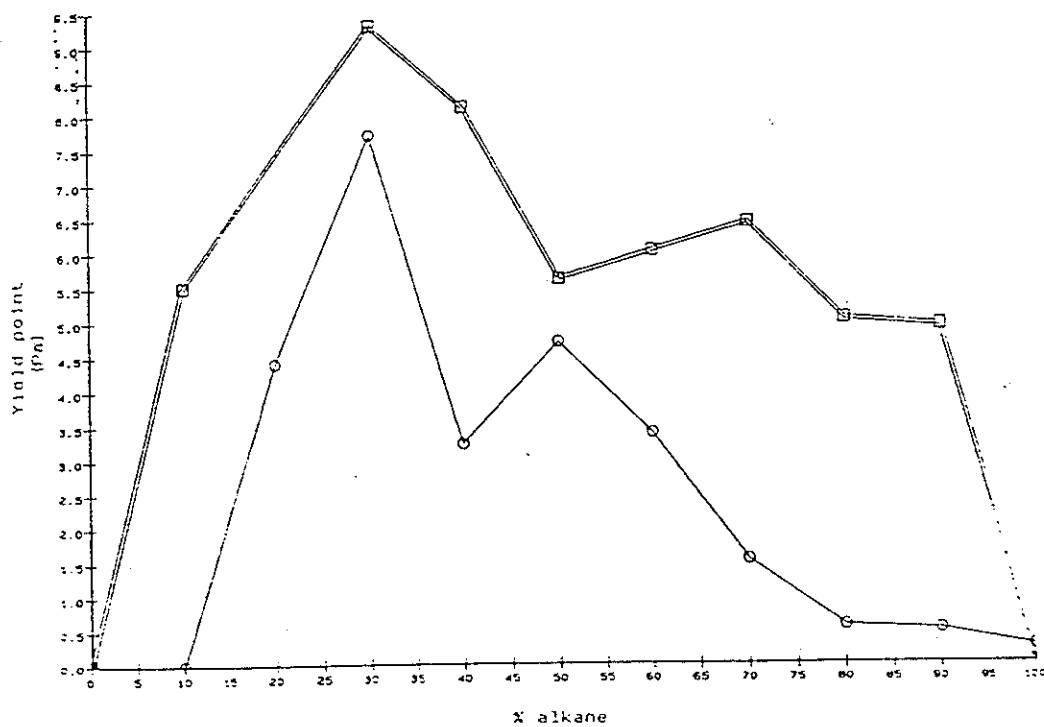


Figure 41: Water content vs % alkane



—□— 0.025 g/mL asphaltene / 0.05 g/mL wax
 —○— 0.1 g/mL asphaltene / 0.05 g/mL wax

Figure 42: Yield point (ppn) vs % alkane



Rheological properties

All the stable emulsions formed during this study exhibited non-Newtonian flow behaviour. Flow curves for mousse (Figure 43) indicate that they behave as pseudoplastic liquids which have a definite yield point and a thixotropic flow behaviour. This complex flow behaviour means that viscosity is extremely dependent upon shear conditions (shear rate and length of time shear is applied). Therefore, a single viscosity number can not properly characterize the fluidity of mousse. Figure 44 demonstrates the effect of shear rate on apparent viscosity.

Figure 43: Flow curve for mousse. Shear stress versus shear rate.

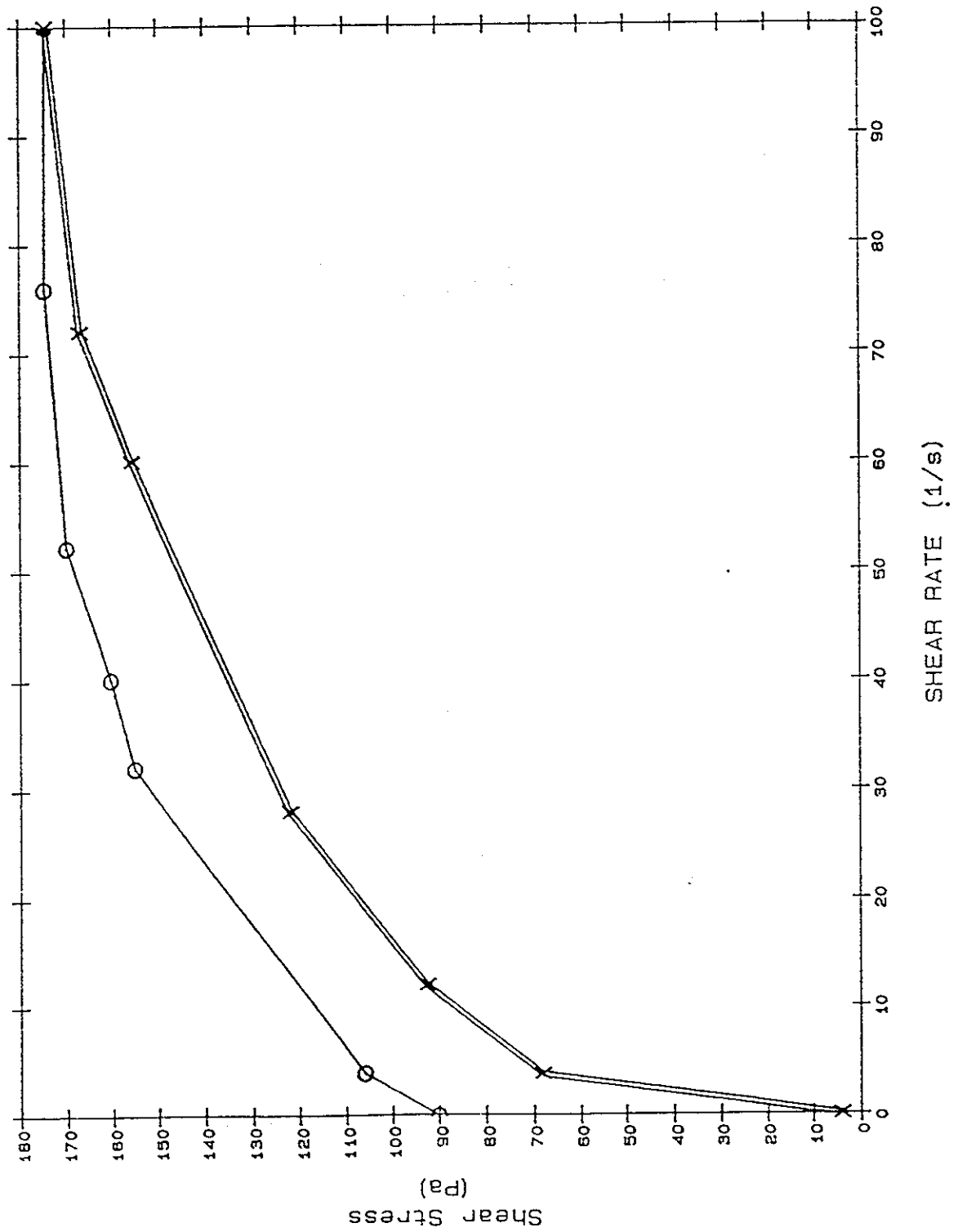
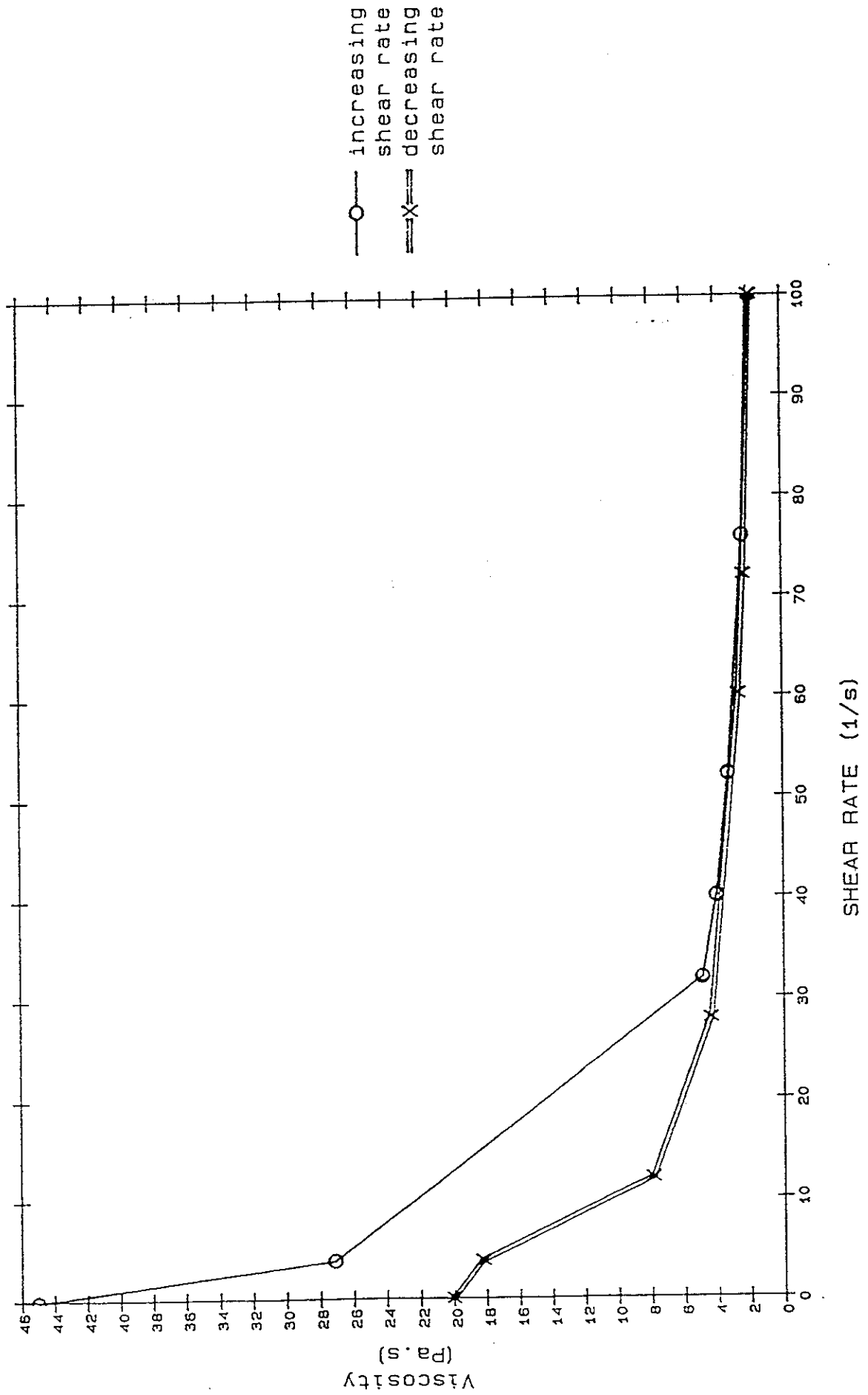


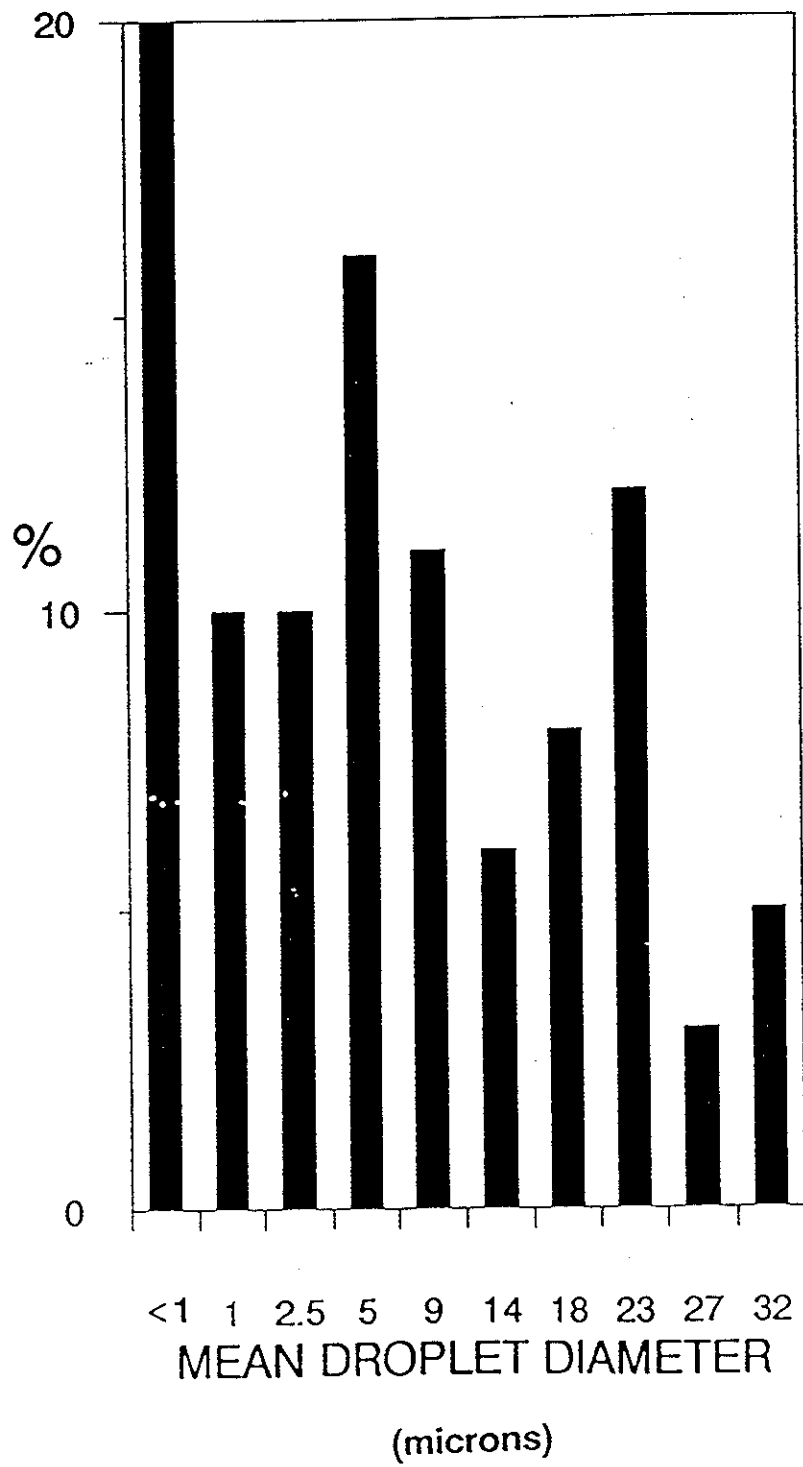
Figure 44: Effect of shear rate on apparent viscosity of mousse.



Droplet size distribution

Figure 45 shows the droplet size distribution for a typical mousse formed by the model oils. The droplet diameters are very heterogeneous and appear to have at least a bi-modal distribution. This multi-modal size distribution means that the water content of emulsions can exceed the theoretical maximum value of 74% which would apply if the droplets had a single modal distribution. In effect, this allows droplets of a smaller size to occupy the gaps between larger droplets, thus creating an extremely dense packing of droplets. Yield point increases as the droplet size distribution shifts to smaller values.

Figure 45: Droplet size distribution.

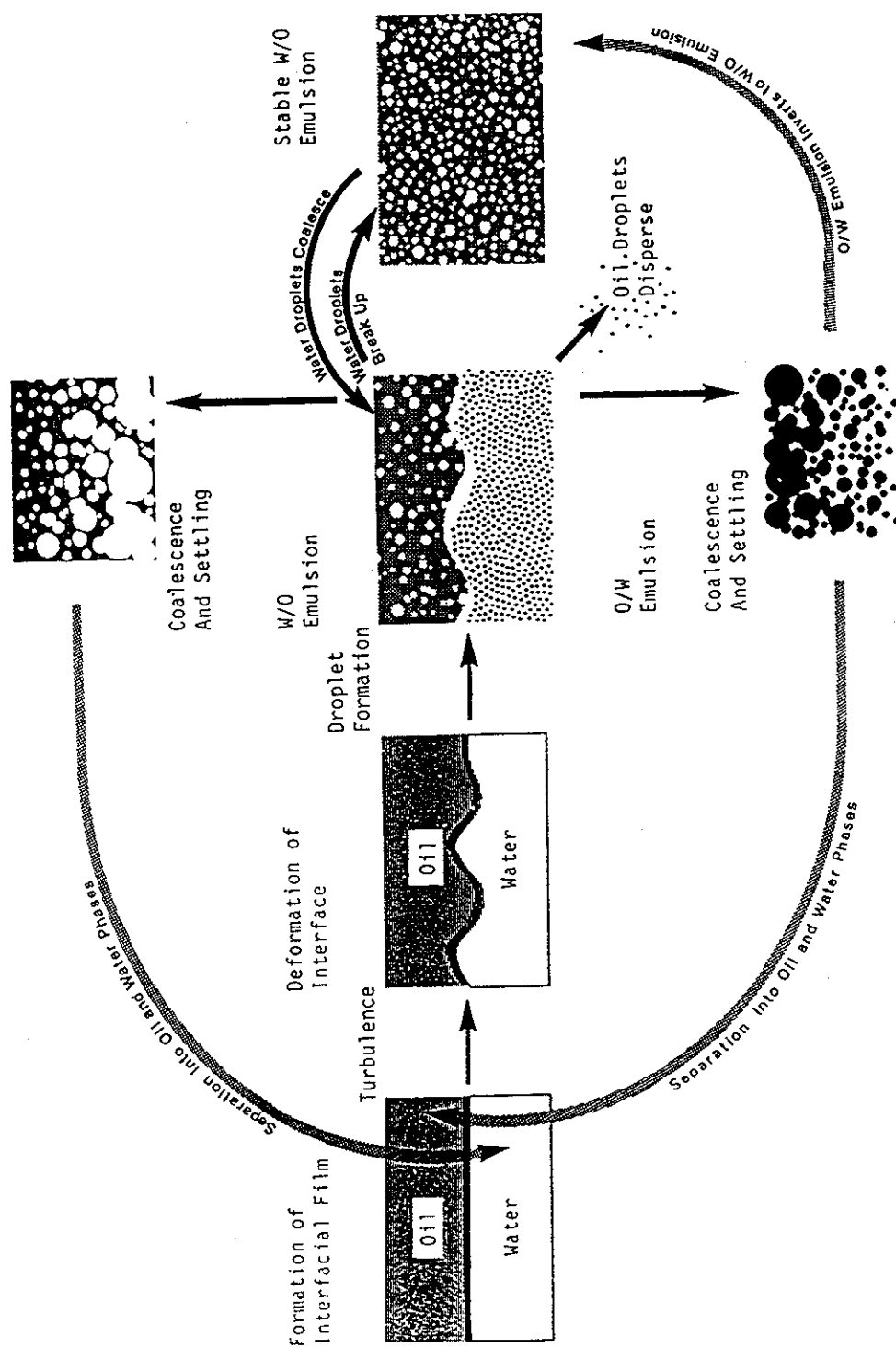


THEORETICAL DISCUSSION

Emulsification, whether it occurs in oil spilled on the ocean or in an industrial setting, is a complicated phenomenon. Many aspects of emulsion formation and stability are poorly understood. Indeed, emulsification itself is not a one-step process but the result of several processes which occur both in succession and simultaneously. A true appreciation of the complexities involved can be obtained by examining Becher's "Encyclopedia of Emulsion Technology" (Becher 1983). This voluminous compilation of work clearly indicates that an extensive amount of research has gone into the study of emulsions for industrial purposes but that many aspects remain unexplained. Studying the emulsification of petroleum is further complicated by the fact that oil is a complex multi-component mixture that undergoes numerous physical and chemical changes as soon as it is spilled. Additionally, limited work has gone into studying the dynamic interaction between oil slick and surface energy. Clearly, the derivation of an all-embracing theory that explains mousse formation is, to say the least, formidable. A brief summation of different aspects of emulsification which are applicable to the formation of water-in-oil emulsions is presented here. More detailed discussion and thermodynamic treatment of the mechanisms involved can be found in Becher's Encyclopedia (Becher 1983).

A stable emulsion is the end-result of several processes. Figure 46 shows a schematic representation of some of the processes involved.

Figure 46: Schematic diagram of processes occurring during emulsification.



Interfacial Film

In order to form an emulsion, an interfacial film must exist between the two liquid phases. This layer is made up of material that has the property of accumulating at the interface between the two liquids. In crude oil, this layer would be made up of indigenous particles, macromolecules, and other interfacially active species. In a mixture such as petroleum, numerous surface-active compounds exist; a list of those cited in the literature is presented in Table 1. In addition to these, other processes such as photooxidation and biodegradation lead to the formation of other surface-active materials.

It is known that a mix of emulsifying agents often leads to more stable emulsions than does a single type of emulsifier (Becher 1983). The presence of mixed emulsifiers can result in a complex formation at the interface. An example of this is the liquid crystalline phase that is formed in certain mixed surfactant systems. Water-in-oil emulsions that are formed by liquid crystalline tend to have semi-solid, gel-like structures similar to crude oil mousse (Tadro & Vincent 1983).

Studies have shown that the interface between crude petroleum and water can be highly viscoelastic and even rigid (Jones 1978; Blair 1980; Eley et al. 1987). There is also evidence to suggest that the interfacial film is not made of one, single layer of material but that it is augmented by a secondary layer (Blair 1960; Hasiba 1968). The more active compounds in oil will migrate and adsorb to the interface, and thus form the primary layer. Less active compounds will then accumulate on top of this primary layer and form a secondary layer.

Sufficient evidence from numerous of studies exists to conclude that the asphaltene, resin and wax fractions constituent a significant part of the interfacial film. Data from this present study clearly indicates that these compounds are most effective as emulsifying agents when they exist as solid particles. However, it should also be realized that when these compounds are in the dissolved state, they can still act as emulsifiers. Dissolved asphaltene and resin compounds can behave as conventional surfactants by lowering the interfacial tension. As well, macromolecules similar to dissolved asphaltenes, resins and waxes, are commonly used as industrial emulsifiers

(Walstra 1980).

Table 1: Compounds in crude petroleum that can be interfacially active

organic sulfur compounds

-sulfides, sulfates, sulfonic acids, sulfones, thiophenes

organic oxygen compounds

-alcohols, ethers, carboxylic acids, carboxylic anhydrides, carboxylic esters, ketones, furans

organic nitrogen compounds

-pyridine, quinoline, pyrrole, indole, cardazole

metal porphyrin complexes

asphaltene and resin fractions

organic and inorganic particles

Initially when oil is spilled, the fresh oil can be considered to be in a stable physicochemical state, that is the waxes, resins, and asphaltenes are either dissolved in the oil or present as suspended micelles. As the oil begins to weather, numerous changes occur in the oil which affect emulsification. Evaporation and dissolution of the light-end compounds causes an increase in oil viscosity and density, both of which generally enhance emulsification. The indigenous emulsifiers have low volatility and aqueous solubility, thus weathering concentrates them in the remaining oil. The loss of volatile compounds also causes a change in the solvency strength of the oil which in turn affects the phase equilibrium of the asphaltenes, waxes and resins. The oil matrix can not maintain these asphaltic compounds in solution and as a result, precipitation occurs. The precipitates have specific gravities of approximately one (Mullins 1990) and therefore, they will quickly concentrate at the oil/water interface. Although these particles are referred to as solids, in-situ they are saturated with oil and collectively they form a semi-solid, tarry-like substance. These same particles are responsible for the troublesome waxy and tarry

deposits found in production pipelines, and the tar layer found between the oil and water deposits in some reservoirs. (Kawanaka et al. 1989, Dickey 1979)

How different components interact during precipitation is still largely unknown. It is likely that co-precipitation occurs and that solid solutions, also known as mixed crystals, are formed (Mochida et al. 1986). Precipitated particles may also flocculate and polymerize (Kawanaka et al. 1989). As well, other liquid entities in the oil may become trapped in the flocculated mass or absorbed onto its surface. These mechanisms could enable hydrophobic material such as wax to contact the interface. Long-term studies on spilled oil have found that the asphaltic content of oil increases faster than would be indicated by the mere loss of evaporated compounds (Frankenfeld 1973; Bobra 1989). This suggests that other compounds are being transformed into asphaltic components. Indeed, asphaltenes are regarded as the final product of petroleum oxidization, and they, themselves, can be further oxidized (Speight 1980).

Water-in-oil Droplet Formation

The mechanism by which water enters the oil phase and ultimately assumes the form of micron-sized droplets is still a phenomenon that remains unexplained. There are two fundamental theories which could explain how water enters oil. Indeed, it is possible that both these mechanisms take place during mousse formation.

One theory is that initially the oil is dispersed into the water, forming an oil-in-water emulsion. If the prevailing conditions are inadequate to maintain the oil droplets in the water column, these droplets will return to the surface where they will flocculate and coalescence. During this process small amounts of water which were trapped between the oil droplets thus become droplets of water within a continuous oil phase. Large droplets would either settle out or be broken down into smaller droplets. This phenomenon where an oil-water emulsion is inverted into a water-in-oil emulsion is referred to as inversion (Becher 1983).

The other theory is that water droplets enter the oil phase and are subsequently broken up in smaller ones. In order for water to enter the oil phase, the interface must be disrupted or deformed to such an extent that droplets forms. Walstra (Walstra 1983) cites four mechanisms which can result in the formation of droplets at an interface. They also examine in detail the forces and parameters involved. Although the mechanisms are discussed in relation with mechanical agitators, one can envision some if not all of these mechanisms occurring on a turbulent ocean surface. Unfortunately, little analysis has been done on how the complex forces of the ocean surface impact the oil-water interface. Disruption or deformation of an interface may take place by:

1. turbulence - Small turbulent eddies may disrupt the interface and shear off droplets.
2. capillary ripples - Any disturbance of the interface will cause ripples to develop and under certain conditions the ripple can break into droplets.
3. Rayleigh-Taylor Instability - This instability occurs when the interface is accelerated perpendicular to its plane from the light phase (oil) into the heavier phase (water). Fingers of water enter the oil and break into globules.

4. Kelvin-Helmholtz Instability - This instability in the interface is formed when the two phases move at different velocities and parallel to the interface. In effect, this is how wind causes waves on water.

It is likely that the initial size of the water droplet that enters the oil is large and that these are then deformed and disrupted into smaller ones by viscous and inertial forces. Walstra (Walstra 1983) presents a thorough discussion of droplet break-up.

Although several studies have examined the relationship between ocean surface energy and dispersion, little has been done to quantify the energy relationship to emulsification. Therefore, it is difficult to deduct which mechanisms of droplet formation and break-up take place in a spill. The spatial and temporal motion of the ocean surface undoubtedly creates a complex shear stress upon the oil-water interface. At the present time, the relative importance of small-scale surface turbulence (such as capillary waves) versus larger scale waves to water-in-oil emulsification remains largely unstudied. As with dispersion, there must be a threshold energy which has to be met in order for emulsification to occur. It is speculated that fine-scale turbulence leads to the deformation of the interface and to the formation of droplets, while large scale waves compress and expand the slick which mixes and distributes the emulsifying agents. Payne et al. (1984) noted that the micro-scale turbulence resulting from the grinding action of ice significantly enhanced the formation of stable emulsions.

Several studies (Blair 1960; Mukherjee and Kushnick 1989; Eley, Hey and Lee 1987) have examined interfacial properties under dynamic conditions. During compression of the interfacial film, the less strongly adsorbed compounds are squeezed out and only the strongly adsorbed material are left behind at the interface. It is believed that macromolecules and solids are irreversibly absorbed. Therefore, asphaltenes, resins and waxes are likely concentrated in the film during compression. Eley et al. (Eley et al. 1987) found that the viscoelastic behaviour of a crude oil's interfacial film exhibited the characteristics of a network structure of densely packed particles.

The movement of surface active compounds in and out of the interface also has other consequences. In an area of compression, the interfacial film would thicken, while in an area of expansion, the film would thin. This causes an uneven concentration of

emulsifiers along the interface. Emulsifiers are concentrated in the thick region and there would be a low concentration in thin regions. This non-uniform concentration would lead to local variations in the interfacial tension which produces a flow from high to low tension regions. This flow of compounds induced by the interfacial tension gradient results in interfacial instabilities that facilitate droplet formation. This phenomenon is known as the Gibb-Macagoni Effect (Walstra 1983). Therefore, oil-soluble emulsifiers that are not irreversible adsorbed to the interface will upon compression be re-distributed into the bulk oil. These emulsifiers can then migrate back to an interfacial region. It is therefore, conceivable that such an emulsifier molecule could participate in the successional formation of numerous water droplets.

Water soluble surfactants are known to be produced by photolysis and biodegradation of oil (Bobra 1989, Connan 1984). During compression of the interface, these compounds would move across the interfacial plane from the oil phase into the water. This would result in an interfacial tension gradient and an instability that also facilitates deformation of the interfacial film and droplet formation.

Emulsion Stability

Emulsions can be stabilized against breakdown by one or more mechanisms. Basically, there are three mechanisms : 1. charge stabilization; 2. steric stabilization; and 3. stabilization by absorbed particles. In a stable mousse, the dominant mechanisms will be the steric mechanism and stabilization by particles. There is no clearly defined dividing line between macromolecules which lead to steric stabilization and particles. Therefore, in a system as complex as crude oil mousse where both mechanisms occur, it would be impossible to differentiate the two.

The stable nature of mousse can be attributed to the effective physical barrier that is created by the interfacial film that surrounds each water droplet. These films have high mechanical strength and can be viscoelasticity. Electron examination of stable crude oil mousse (Eley et al. 1976) showed that the film layer had a thickness in the range of 100 to 200 nm. This thickness corresponds well to an estimated thickness of a film made-up of precipitated waxes and asphaltenes. (The estimation is based on a given wax and asphaltene concentration of 4.8% and 3.05% respectively, and a mousse containing 60% water with an assumed interfacial area of $2 \times 10^5 \text{ m}^2$.) Calculations using results from this present study indicate that when asphaltenes are the emulsifying agent, a film with a minimum average thickness of 30 nm must surround each water droplet. For a mousse with a water content of 80% and a droplet size distribution as shown in Figure 45, this means that the oil must contain roughly 2.5% asphaltenes, and that the amount of asphaltene in the interfacial film will be approximately 3 mg/m^2 . For stable emulsions formed where the emulsifying agents are primarily waxes, the minimum film thickness is 60 nm. These simple calculations do not take into account that the interfacial films of neighbouring water droplets may share particles and molecules, thus increasing the effective thickness of the films.

CONCLUSIONS

The results from this study demonstrate the importance that the physical state of an emulsifying agent has upon its ability to stabilize emulsions. It was found that to be effective emulsifiers, asphaltenes, resins and waxes must be in the form of finely divided, sub-micron particles. The chemical composition of the oil determines not only the amount and size of these particles but also their composition and their wetting properties. All these factors were shown to have an influence upon the emulsification process.

Asphaltenes and resins, by themselves and in combination, were effective emulsifying agents. Model oils containing only wax as the emulsifying agent did not form stable emulsions. But the addition of a nominal amount of asphaltenes, an amount insufficient by itself to produce emulsions, to oils containing wax, lead to the formation of stable emulsions. This indicates that different emulsifying particulates can synergistically interact to stabilize emulsions.

The solubility/precipitation behaviour of asphaltenes in model oils follows the solubility theory as described by the Hildebrand-Scatchard equation. Therefore, it could potentially be adapted to model the precipitation behaviour of indigenous petroleum emulsifiers as spilled oil weathers, and thus be used to predict the physicochemical conditions in oil which favour mousse formation.

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